IMPACT OF SOIL ORGANIC MATTER ON GROUNDWATER CONTAMINATION RISKS FOR ETHANOL AND BUTANOL BLENDED GASOLINE

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ABSTRACT

This work examined the impact of soil organic matter (SOM) on the sorption, phase distribution and transport of ethanol and butanol blended gasoline vapours after release. Microcosm and mini-lysimeter experiments were conducted using sand with varying SOM and moisture contents. Synthetic gasoline alone and blended with 10 - 20% ethanol and 10 - 20% butanol by volume, referred to as UG, E10 - E20 and B10 - B20, respectively, were used. Results from the UG were used as the benchmark to assess the impact of ethanol and butanol on gasoline compounds. The findings of this work illustrate the likely behaviour of gasoline compounds at the beginning times of a gasoline spill or leak.

The addition of alcohol to gasoline altered the behaviour of the gasoline compounds in the vadose zone in several ways. Firstly, it reduced the sorption of the gasoline compounds by soils. This effect was greatest on the first day of a spill and affected the gasoline compounds in decreasing order of hydrophobicity. Secondly, it altered the mass distribution of the gasoline compounds between the vadose zone phases to higher mass compounds in the mobile phases (soil air and soil water) and lower mass compounds in the immobile soil solid phase, suggesting higher risk of groundwater contamination with an increasing content of alcohol in the gasoline. Thirdly, it increased the vapour phase transport of the gasoline compounds from the source zone to the groundwater zone. These three impacts were generally greater for ethanol than butanol. The sorption coefficients (K_d) of E20 gasoline compounds were reduced by 54% for alkanes, 54% for cycloalkanes and 63% for the aromatics, while the K_d of B20 gasoline compounds decreased by 39% for alkanes, 38% for cycloalkanes and 49% for aromatics. This implies that the use of ethanol as

gasoline oxygenate could result in greater risk of groundwater contamination with gasoline compounds than the use of butanol after spills.

The SOM enhanced the sorption of alcohol-blended gasoline compounds in soils. This impact was similar for ethanol and butanol blended gasoline as the K_d of B20 and E20 were equally increased by 7 times for aromatics, 4 times for cycloalkanes and 2 times for alkanes, for 0 to 5% increase in the SOM fraction of sand. Although SOM enhanced the sorption of alcohol-blended gasoline, its sorptive capability was not fully realised compared with the sorption of the UG compounds. Also, it did not alter the order of groundwater contamination risk for the ethanol and butanol blended gasoline. Thus, the K_d values for all gasoline compounds for all the SOM fractions tested, including $0\%f_{om}$, $1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$, were in the order of UG>B20>E20, indicating greater risk of groundwater contamination for the ethanol-blended gasoline after a spill or leak regardless of the SOM content of the soil.

The increase in the water content of soil reduced the sorptive capability of SOM and affected the overall mass distribution of gasoline compounds between the soil solid, soil air and soil water phases estimated with values of Henry's law constant from the literature. This indicates that the degree of gasoline retention in the vadose zone by SOM could differ during the dry summer and wet winter seasons. This effect was greater for ethanol than butanol. Thus, in all seasons, the amount of gasoline compounds retained by SOM in the vadose zone is likely to be higher for butanol-blended gasoline than ethanol-blended gasoline.

Overall, this study indicates that the use of high ethanol volume in gasoline to combat climate change may put the groundwater at greater risk of

contamination after spills or leakages from storage. Therefore, to successfully reduce greenhouse gases emissions via high alcohol volume in gasoline and still protect the world's groundwater resource, this study suggests the use of butanol is more benign than ethanol.

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AFFIRMATION

The work presented in this thesis was undertaken at the Department of Chemical and Environmental Engineering, University of Nottingham, between August 2009 and July 2012. This thesis is the result of my own work. Neither the present thesis, nor any part thereof, has been submitted previously for a degree to this or any other university.

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$B0\,and\,E0$	0% alcohol + 100% gasoline
$B10$	10% butanol + 90% gasoline
$B20$	20% butanol + 80% gasoline
$E10$	10% ethanol + 90% gasoline
$E20$	20% ethanol + 80% gasoline
θ_a	Air-filled porosity
ρ	Bulk density
C_s	Concentration of gasoline compound in soil solids
C_w	Concentration of gasoline compound in soil water
H	Henry's law constant
M_a	Mass of gasoline compound in soil air
M_s	Mass of gasoline compound in soil solids
M_w	Mass of gasoline compound in soil water
M_L	Mass lost via sampling
K_{ow}	Octanol-water partition coefficient
ρ_s	Particle density
n	Porosity
R	Retardation factor
$0\% f_{om}$	Sand + 0% organic matter
$1\% f_{om}$	Sand + 1% organic matter
$3\% f_{om}$	Sand + 3% organic matter
$5\% f_{om}$	Sand + 5% organic matter
f_{om}	Soil organic matter fraction
θ	Soil water content
K_d	Sorption distribution coefficient

M_t	Total mass of gasoline compound injected into microcosm
θ_t	Total porosity
M_{ts}	Total soil mass
V_{ts}	Total soil volume
C_a	Vapour phase concentration of gasoline compound in microcosm
V_a	Volume of air in microcosm
V_w	Volume of water in microcosm
θ_v	Volumetric water content
θ_w	Water-filled porosity

LIST OF ABBREVIATIONS

BS	British Standard
EBTP	European Biofuels Technology Platform
EPCEU	European Parliament and the Council of the European Union
FC	Field Capacity
GC	Gas chromatography
GC-FID	Gas chromatography with Flame Ionization Detector
GWO	groundwater outlet tube
HOC	Hydrophobic Organic Compound
IP	Injection Port
ITRC	Interstate Technology & Regulatory Council
LOI	Loss on ignition
MCH	Methylcyclohexane
MCP	Methylcyclopentane
MS	Mass spectrometer
MW	Molecular weight
NAPL	Non-aqueous Phase Liquid
OD	Oven Dry
OEHHA	Office of Environmental Health Hazard Assessment
OTA	Office of Technology Assessment
SA	Surface Area
SOM	Soil organic matter
SP	Sampling Port
SSA	Specific Surface Area
TPV	Total Pore Volume
UG	Unblended gasoline
USDA	United State Department of Agriculture
USEPA	United State Environmental Protection Agency

USGS	United State Geological Survey
UST	Underground Storage Tank
UTTU	Underground Tank Technology Update
WIR	Water Infiltration Rate
WRC	Water Retention Capacity

CHAPTER ONE

1. INTRODUCTION

1.1 Driving force of the study

Alcohol-blended gasoline is widely used as fuel and its release into the environment is likely. After an accidental release to the soil, the persistence of gasoline compounds in the vadose zone, their migration to groundwater and the scale of contamination expected in the groundwater are problems of particular environmental concern. This requires the knowledge of the sorption characteristics of the gasoline compounds in the presence of the alcohol as well as the knowledge of the soil type and characteristics (Site, 2001). Such knowledge will be vital in making informed decisions regarding the suitability of remediation options for different contamination scenarios. It will also be crucial for the successful development and applications of fate and transport models to practical situations. Although this knowledge exists for gasoline, little is known about butanol-blended gasoline and the impact of soil organic matter (SOM) on ethanol or butanol blended gasoline.

Presently, ethanol is the most commonly used gasoline oxygenate in the UK and other countries of the world, including United States and Brazil (Hahn-Hägerdal et al., 2006). It is added at up to 10% by volume in gasoline in Australia, USA and England and as high as 25% in Brazil (Niven, 2005; Powers et al., 2001b). Since the phase out of methyl tertiary butyl ether (MTBE) as gasoline oxygenate in the early 2000s, the utilization of ethanol as gasoline oxygenate has witnessed a consistent increase as shown in Figure 1.1. This increase is driven mainly by legislation, such as

the Clean Air Act and the Energy Independence and Security Act (EPCEU, 2003; USEPA, 2011a). The trend is likely to continue as new legislations and policies requiring more biofuels to be used are gradually coming into effect (Powers et al., 2001b). For instance, The U.S. Environmental Protection Agency has recently granted a waiver allowing the increase in ethanol content of gasoline from 10 to 15% for light-duty vehicles of model year 2001 and newer (USEPA, 2011c). In Brazil, the government mandated a rise in the blend from 20 to 25% ethanol for normal vehicles, and 100% ethanol for flexible-fuel vehicles (Niven, 2005). The European Union main members are projecting to consume 6.3 billion litres of ethanol fuel by 2020 (Szklo et al., 2007), up from 4.3 billion litres in 2009 (Biofuels-Platform, 2010). In India, the government implemented a program that will increase ethanol volume in gasoline to 10% by 2015, and in China, the government targets to increase the volume of ethanol in gasoline from 7.7 to 15% (Szklo et al., 2007).

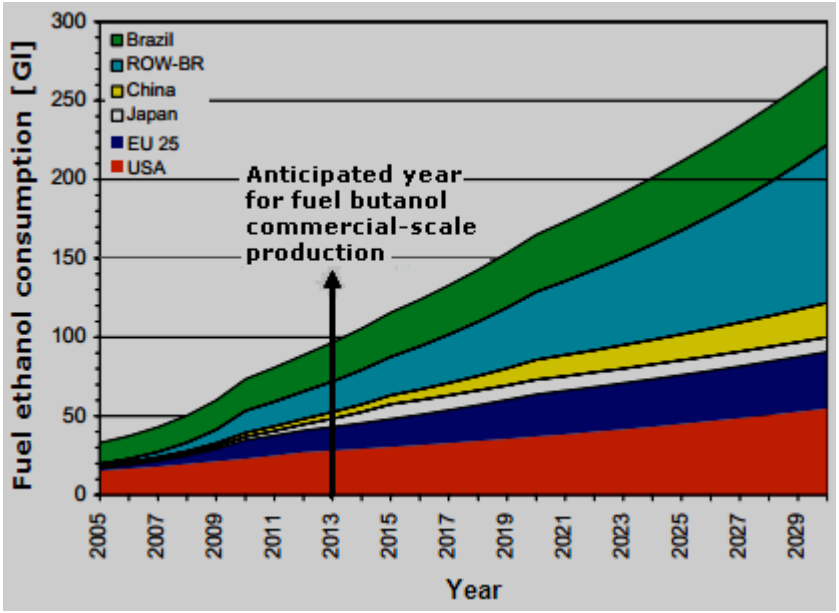

Figure 1.1 Estimated consumption of fuel ethanol and the intended use of fuel butanol (Adapted from Walter et al., 2008).

Interest in other fuel alcohols, such as butanol (Figure 1.1), has grown recently due to its advantages over ethanol as discussed in Section 2.3.3. Studies on butanol and butanol-blended gasoline have so far only concentrated on biodegradation where studies indicate that butanol is readily biodegraded (Fairbanks et al., 1985; Mariano et al., 2009) but can affect the biodegradation of gasoline compounds in soil (Gomez and Alvarez, 2010; Mariano et al., 2009). Therefore, it has become imperative to investigate how the desired butanol-blended gasoline will alter the concentrations of gasoline compounds that may migrate to the groundwater after spills relative to ethanol-blended gasoline before its adoption for public use.

The alcohol-blended gasoline issue towards groundwater contamination after spills has been accelerated after alcohol has been considered as a suitable fuel oxygenate, since it addresses air quality objectives without itself affecting groundwater quality compared with MTBE (Beller et al., 2001). However, studies on the impact of alcohol on gasoline compounds, especially with 10 and 20% ethanol blends, have shown that ethanol affects the infiltration, distribution, sorption and biodegradation of gasoline compounds in sandy soils (Lawrence et al., 2009; Mackay et al., 2006; McDowell and Powers, 2003; Österreicher-Cunha et al., 2007; Österreicher-Cunha et al., 2009; Powers et al., 2001a; Powers and McDowell, 2001).

Although previous sorption studies may have shed light on the contribution of SOM to the overall sorption of hydrophobic organic compounds (HOCs) by soils, the findings may not be applicable to gasoline and gasoline blends due to the single HOC generally used in those studies. Such single HOC lacks the intermolecular interactions that exists amongst gasoline

compounds (Lawrence et al., 2009) and has been found to result in overestimation of vapour concentrations and reduction in interfacial and surface tensions (Karapanagioti et al., 2004; Powers and McDowell, 2001). Gasoline is a complex mixture of volatile and semivolatile hydrocarbons, predominantly composed of paraffins, olefins, naphthenes and aromatics (Powers et al., 2001b; Speight, 2002). Thus, this study has concentrated on a hydrocarbon mix close to actual gasoline as highlighted in Section 2.3.2. More so, the addition of alcohol, which is highly miscible with water, as an oxygenate to gasoline will further impact the characteristics of the gasoline as well as the intermolecular interactions amongst the gasoline compounds as discussed in Sections 2.2.4, 2.2.5 and 2.3.3.

Another physical property that may affect the sorptive capability of SOM that has been studied is soil water content. Previous studies have shown that the water content of a soil can affect the sorption and transport of organic contaminants in the vadose zone (Acher et al., 1989; Johnson and Perrott, 1991; Ong and Lion, 1991; Site, 2001; Smith et al., 1990; Steinberg and Kreamer, 1993). These studies argued that the increase in the water content of a soil could reduce the available surface area of the soil by filling some of the pores. Because water can substantially reduce the surface activities of inorganic surfaces by occupying the high-energy sites (Site, 2001), it is possible that increasing the water content of a soil could also decrease the SOM sorptive capability. This may especially be important as the fuel alcohol levels are increased (EPCEU, 2003; Powers et al., 2001a; USEPA, 2011a). Understanding the degree of this impact will be useful in predicting the behaviour of alcohol-blended gasoline in the soil during dry summer and wet winter.

As a hydrophilic compound, alcohol may partition into the aqueous phase, thereby increasing the solubility of gasoline in water, as well as reducing surface and interfacial tensions. Consequently, alcohol can alter the overall interactions between gasoline, soil water and soil particles. Although mounting evidence have shown that hydrophobic organic compounds, such as gasoline compounds, have high octanol-water partition coefficient (K_{ow}) and will tend to be retained by SOM in the soil (Celis et al., 2006; Chen et al., 2007; Chiou, 2002; Guo et al., 2010; Joo et al., 2008; Liu et al., 2008; Marchetti et al., 1999; Wang et al., 2008a; Weber et al., 2001), no study has been conducted to investigate the impact of SOM on the sorption of alcohol-blended gasoline in the vadose zone. This has been a major aim of this study. Thus, it is anticipated that the findings of this research may be the new tool needed for predicting spill behaviour in future renewable fuel formulations. Such findings could be of significant importance to regulators as well as a range of industries across the UK and abroad.

1.2 Aim and objectives

The main aim of this study was to investigate the impact of SOM on the sorption, phase distribution and transport of ethanol and butanol blended gasoline vapours in the vadose zone after spills.

The objectives of this study were to:

- Design, fabricate and commission a 14 cm x 40 cm mini-lysimeter system that simulates the vadose zone during spills.
- Assess the impact of ethanol and butanol on the sorption, phase distribution and transport of the vapour phase of gasoline compounds in the vadose zone.

- Investigate the contribution of SOM to the overall sorption, phase distribution and transport of the vapour phase of ethanol-blended and butanol-blended gasoline compounds in the vadose zone.
- Study the effects of ethanol and butanol on the sorptive capability of SOM for gasoline compounds.
- Examine the impact of soil water content on the sorptive capability of SOM for ethanol-blended and butanol-blended gasoline compounds.
- Determine the impact of SOM on the vapour phase transport of ethanol-blended and butanol-blended gasoline compounds to the groundwater zone.

1.3 Thesis overview

This thesis presents a laboratory study to investigate the impact of SOM on the sorption, phase distribution and transport of ethanol-blended and butanol-blended gasoline vapours after release. Chapter 1 has presented the driving force of the study as well as the aim and objectives. Chapter 2 contains a review of related literature, and covers the contamination of soil and groundwater systems, sources and effects of soil and groundwater contaminations, fate of contaminants in the subsurface environment, contamination monitoring techniques, contaminants detection and quantification equipment, and research justification. Chapter 3 describes the materials, techniques, and equipment employed for each experiment performed in this study. It also describes the design of the novel laboratory system (mini-lysimeter) used. The results from this study are presented in Chapters 4 to 8. Chapter 4 provides the baseline measurements from the laboratory systems used. Chapter 5 contains all results from the ethanol-blended gasoline experiments, including impact of ethanol on the sorption

and transport of the vapour phase of gasoline compounds, impact of SOM on the sorption and transport of the vapour phase of ethanol-blended gasoline compounds, and ethanol and soil water content effects on the sorptive capability of SOM for gasoline compounds. Chapter 6 comprises all results from the butanol-blended gasoline experiments, similarly presented as the results for the ethanol-blended gasoline experiments for a fair comparison. Chapter 7 evaluates the sorption and transport of the ethanol-blended and butanol-blended gasoline vapours using the unblended gasoline vapours as the standard. Chapter 8 presents the conclusions of this study and recommendations on how this work can be extended to fully aid a complete understanding of the fate of alcohol-blended gasoline in the subsurface environment.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

Numerous studies have been conducted on the fate and transport of gasoline compounds in the subsurface environment due to the widespread and frequent use of gasoline and the possibility of its release to the environment from surface spills, subsurface leaks and transportation accidents (OEHHA, 1999). These studies have identified that after the release of gasoline to the soil, the persistence of the gasoline compounds in the vadose zone, their migration to groundwater and the evaluation of the scale of contamination expected in the groundwater are problems of particular environmental concern, which require the knowledge of the sorption characteristics of the gasoline compounds, their proportion within the gasoline composition, as well as the knowledge of the soil type and characteristics (Meyers, 1999; Site, 2001). Therefore, the review of literature in this study focused on the release of gasoline to the soil and the properties of gasoline and soil that affect the fate and transport of gasoline compounds in the vadose zone as well as the changes in gasoline and soil properties in the presence of alcohol.

2.2 Contamination of soil and groundwater systems

Soil and groundwater are major parts of the natural environment alongside air and surface water, and are generally considered contaminated when they contain substances that, when present in sufficient quantity or concentrations, are likely to cause harm directly or indirectly to humans,

plants, animals, the environment or other targets such as construction materials (Harris et al., 1996). The Groundwater-Foundation (2011) noted that a major source of groundwater contamination occurs when man-made products, such as gasoline, oil and chemicals, get into the groundwater and cause it to become unsafe and unfit for human use.

After a spill, the contaminants can reach receptors via various pathways, such as direct contact, inhalation, ingestion, downward migration and evaporation as outlined in Figure 2.1. The degree of threat posed by contaminants travelling along these pathways is usually one of the many key factors that determines the course of action required to minimize or eliminate the threat (Yong, 2001). The presence of alcohol is expected to have a major effect on the transport of contaminants to groundwater as discussed later in Section 2.4.3.1.

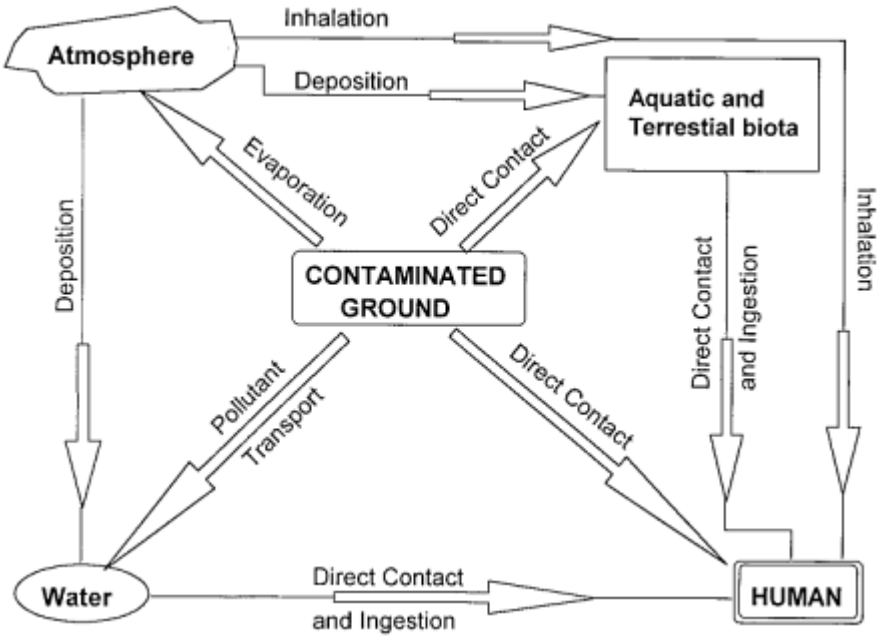

Figure 2.1 Pathways from contaminated soil to potential receptors (Adapted from Yong, 2001).

2.2.1 Sources of soil and groundwater contaminations

The contamination of soil and groundwater may occur naturally or as a result of human activities (USEPA, 2011b; Yong, 2001). A study conducted by the Office of Technology Assessment (OTA) recognized more than 30 sources known to contaminate soil and groundwater (Rail, 2000). These sources include industrial and transport, agricultural, domestic, municipal, and natural sources. This research focuses on accidental spill during transport and industrial storage and these are explained below.

2.2.1.1 Spills during transport and industrial storage

Accidental spills during transport are high possible sources of soil and groundwater contaminations by gasoline and other petroleum products (USEPA, 1994). A large volume of petroleum products are transported from one place to another by truck, ship, rail and aircraft. Hence, accidental spills of these materials are commonplace. It has been estimated that about 16,000 spills, ranging from a few to several millions of gallons occur each year in U.S alone (USEPA, 1994). In Russia, industrial sources of groundwater contamination have been reported to contribute to 42% of the total contaminated sites (Zektser, 2000). Figure 2.2 shows a typical surface spill of gasoline and the processes controlling its movement in the subsurface. After a spill, the gasoline will move through the unsaturated zone where a fraction of it will be retained by capillary forces in the soil pores. This depletes the gasoline volume until either movement ceases as for a small spill or the capillary fringe is reached for a large spill where groundwater contamination becomes a concern. However, it is still unclear how these processes will be impacted if alcohol is added to the gasoline and how the SOM content of the soil will dictate the appropriate response for different site conditions.

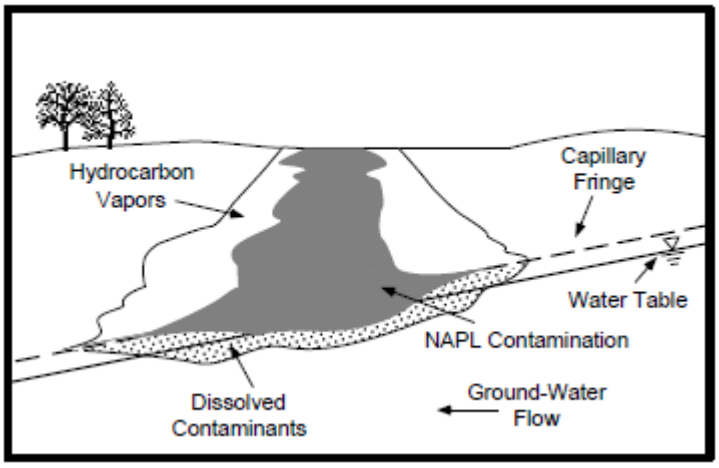

Figure 2.2 Migration of spilled nonaqueous phase liquid (NAPL) (Adapted from Newell et al., 1995).

Leakage from underground storage tanks and pipelines as illustrated in Figure 2.3 is a growing soil and groundwater contamination sources of substantial consequence (Day et al., 2001; Nadim et al., 2001; USEPA, 1994; Zektser, 2000). These facilities store billions of gallons of gasoline and other petroleum products that are used for industrial and transportation purposes. Although pipes and tanks are subject to structural failures arising from a wide variety of causes (Rail, 2000), recent studies have shown that corrosion is the frequent cause for underground storage tanks and pipelines leakages (Rail, 2000; USEPA, 1994). According to Nadim et al. (2001), spills and overflows, loose fittings on top of the tanks, corrosion of tanks and their piping systems, poor installation, and movement of tanks due to land subsidence are among major factors contributing to the failure of underground storage tanks and their piping systems. It has been estimated that about 50% of oil storage sites (Zektser, 2000) and about 35% of all underground storage tanks (USEPA, 1994) in the United States leaks. Unfortunately, these leaks are difficult to detect early (USEPA, 1994; Zektser, 2000). They are usually detected when havoc has been done to the soil and groundwater, and to the

environment at large. Since alcohol is more corrosive than gasoline (see Section 2.4.4) the addition of alcohol to gasoline will cause more leakages of underground storage tanks and pipelines. This implies that the subsurface leaks of alcohol-blended gasoline are likely at gasoline stations. Thus, understanding the behaviour of alcohol-blended gasoline in vadose zones with varying SOM is vital in designing a suitable remediation strategy for a specific site.

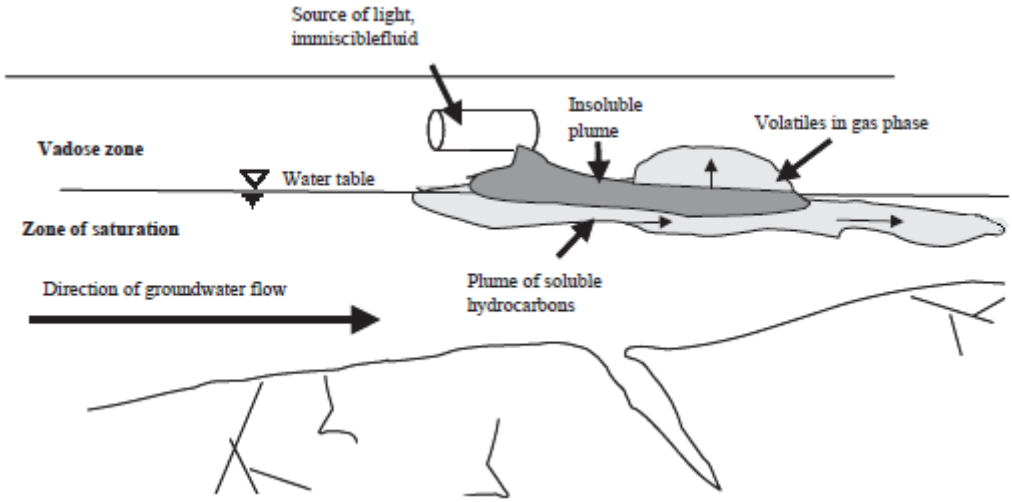

Figure 2.3 Leaking underground storage tank as a potential source of soil and groundwater contamination (From Vallero, 2004).

Soil types, soil properties and contaminant properties play a significant role in the fate of contaminant in the subsurface environment following a spill during transportation or storage. According to Graham and Conn (1992), the effect of soil type on the retention of organic contaminants accounted for more than 80% of the total variation in their retention. Soil properties, such as organic matter (Chen et al., 2007; Joo et al., 2008; Serrano and Gallego, 2006; Shi et al., 2010; Site, 2001; Sparks, 1989; Wang et al., 2008a), water content (Acher et al., 1989; Site, 2001), surface area and cation exchange capacity (Site, 2001), have all been reported to affect

contaminants fate in the subsurface. According to Liu et al. (2008), soil and contaminant properties, particularly the SOM content of soil, the soil nature, the contaminant hydrophobicity and the contaminant molecular structure all affect the retention of organic contaminants in the vadose zone. As reported by Huling and Weaver (1991), the distribution of a contaminant between the vadose zone phases is highly site specific and dependent on the characteristics of both the soil and the contaminant. Also, Site (2001) noted that the distribution of a contaminant between the soil solid and soil water phases and the type of interaction that occurs between the phases, depends on the nature of the soil as well as the physicochemical features of the contaminant. The latter will change significantly with increasing alcohol content in the gasoline as discussed later in Section 2.4.2. Yu (1995) reported that the interphase processes experienced by the contaminants in the vadose zone are also affected by geologic soil properties of the vadose zone and the physicochemical properties of contaminants. In addition, Mercer and Cohen (1990) found that the behaviour of contaminants in the subsurface environment depends on fluid properties such as interfacial tension, viscosity, density, volatility (or vapour pressure) and solubility. Therefore, the next three sections are dedicated to soil types, soil properties and contaminant properties.

2.2.2 Soil types

Soil is defined as an assemblage of discrete particles in the form of a deposit, usually of mineral composition, but sometimes of organic origin, which can be separated by gentle mechanical means and that includes variable amount of water and air (BS1377-1, 1990). Soil plays a major environmental role as a bio-physico-chemical reactor that decomposes dead biological materials and recycles them into nutrients for the continual

regeneration of life on earth (Hillel, 1998). It is formed initially through disintegration and decomposition of rocks by physical and chemical processes, and is influenced by the activity and accumulated residues of numerous microscopic and macroscopic plants and animals. The nature and structure of a given soil depends on geological processes, such as the breakdown of the parent rock, transportation to site of final deposition, environment of final deposition, and subsequent conditions of loading and drainage that formed it. As a result, soil is a complex mixture of different inorganic and organic materials that has been used for their classification into loamy soil, clayey soil, sandy soil, silty soil, chalky soil and peat soil (Buol et al., 2003). These soils have different interactions with hydrocarbon contaminants as discussed later in Section 2.4.2 due to their different properties as listed below.

Loamy soils: These are considered to be the perfect soil, a mix of 20% clay, 40% sand, and 40% silt. Characteristically, they drain well yet retain suitable amount of moisture. Due to mix variations loam can range from fertile soils full of organic matter, to densely packed sod.

Clayey soils: Typically composed of very fine and flaky particles with few air-filled voids, and are thus hard to work and often drain poorly. Clay soils are greasy and sticky when wet and hard when dry. They form a heavy mass, which makes it difficult for air and water to migrate through the soil.

Sandy soils: They generally have a grainy texture. The particles are visible to the naked eye. They retain very little water but high aeration. They are prone to over-draining, and summer dehydration. Sandy soils are often very acidic.

Silty soils: Comprised mainly of intermediate sized particles and are considered to be among the most fertile soils. They are fairly well drained and retain more moisture than sandy soils, but are easily compacted. Silt particles become dusty when dry.

Chalky soils: These are largely made up of calcium carbonate and usually very alkaline. They are usually light brown in colour and contain large quantities of stones of varying sizes. Chalky soils hold little water and dry out easily.

Peat soils: They are mainly organic matter (≈100%) and usually very fertile. The void ratio of peat soils ranges between 9, for dense amorphous granular peat, and up to 25, for fibrous peat (Bell, 2000). Peat soils are prone to retaining excess water.

2.2.3 Soil properties affecting fate and transport of contaminants

Some soil properties provide significant sets of reactions and interactions between soils and contaminants, and thus influence the fate and transport of contaminants within the soil (Yong, 2001). These soil properties include particle density, particle size distribution, specific surface area, bulk density, porosity, water content, and organic matter as discussed below.

2.2.3.1 Particle density (ρ_s)

Particle density is the average mass per unit volume of the solid particles in a sample of soil (BS1377-1, 1990). It is also expressed as the ratio of the total mass of the solid particles to their total volume excluding voids and

water (Burke et al., 1986). Typical values for soils range from 2.5 to 2.8 g/cm^3 with 2.65 g/cm^3 being representative of many soils. Generally, surface soils usually have lower particle density than sub-soils due to the presence of organic matter, which weighs much less than an equal volume of mineral solids (Burke et al., 1986).

2.2.3.2 Particle size distribution

Particle size distribution is the percentages of the various grain sizes present in a soil as determined by sieving and sedimentation (BS1377-1, 1990). Particle size distribution is an essential physical property of the soil and defines the soil texture. The particle sizes present and their relative abundance in a soil influence most physical properties of the soil. For example, it has been reported that the sorption coefficient (K_d) values for diuron and 2,4,5-trichlorophenoxyacetic acid increased with decreasing soil particle size (Nkedi-Kizza et al., 1983). Also, the retention of contaminants by soils has been shown to increase with decreasing soil particle size (Adam et al., 2002). In the British soil classification system, soils are classified according to particle size, and the groups further divided into coarse, medium and fine as shown in Table 2.1 (BS1377-1, 1990; BS5930, 1981). Hence, the particle size distribution of a soil dictates to a large extent the transport of contaminants in the soil.

Table 2.1 British soil classification based on grain size (From BS5930, 1981).

Very coarse soils	BOULDERS		> 200 mm
	COBBLES		200 - 60 mm
Coarse soils	**G** GRAVEL	coarse	60 - 20 mm
		medium	20 - 6 mm
		fine	6 - 2 mm
	S SAND	coarse	2.0 - 0.6 mm
		medium	0.6 - 0.2 mm
		fine	0.2 - 0.06 mm
Fine soils	**M** SILT	coarse	0.06 - 0.02 mm
		medium	0.02 - 0.006 mm
		fine	0.006 - 0.002 mm
	C CLAY		< 0.002 mm

The size of soil particles can be determined using different methods. These methods include dry sieving, wet sieving and sedimentation. Both wet sieving and sedimentation are carried out on extremely fine particles below 45 μm. Dry sieving analyses is typically carried out on particles >60 μm. These methods are described elsewhere (BS1796-1, 1989).

2.2.3.3 Specific surface area

The specific surface area (SSA) of a soil reflects the surface area available for adsorption (Site, 2001). The SSA of soil is an important factor in contaminant adsorption, water absorption, soil strength, and soil transport properties. For example, Site (2001) reported that the K_d values for benzene, toluene and xylenes were lower in kaolinite (SSA = $3*10^4$ m^2/kg) than in illite (SSA = 10^5 m^2/kg) and montmorillonite (SSA = $8*10^6$ m^2/kg), indicating that an increase in the SSA of soil could result in an increase in

the K_d of gasoline compounds. However, as discussed later in Section 2.4.2, the presence of alcohol could significantly change the sorption phenomenon of the SSA for contaminants by reducing the hydrophobicity of the contaminants. The SSA varies widely among soils because of differences in mineralogical and organic composition and in particle size distribution. For example, the SSA of soils have been reported to vary from $<10^4$ m^2/kg for coarse (sandy) soils to $>2.5*10^4$ m^2/kg for fine (clayey) soils (Sumner, 2000). The SSA is expressed either by surface area divided by mass (S_m) or surface area divided by volume (S_v). However, since S_v changes with soil compaction the S_m is normally used.

The SSA of a soil can be determined using different methods, including calculation from particle size distribution, gas permeability and adsorption of substance (Yong, 2001). However, in most laboratories the SSA of soil is measured by adsorption, usually of N_2, using the Brunauer-Emmett-Teller (BET) isotherm. This method has the advantage of measuring the surface of fine structures and deep texture on the soil particles.

2.2.3.4 Bulk density (ρ)

Bulk density is the mass of solid particles of soil per total volume, including voids (BS1377-1, 1990). It is used to quantify the state of compaction and the amount of pore space in a soil, and is expressed by Equation [2.1]:

$$\rho = \frac{\text{mass of solids}}{\text{volume of solids and voids}} \qquad [2.1]$$

Bulk density changes with the packing of the soil particles. Generally, sand pack more closely and has less pore space than loam and clay, with bulk

density values ranging from 1.51 to 1.87 g/cm^3 for sandy loam to gravelly sand compared to bulk density values of 1.34 g/cm^3 for loam and 1.18 g/cm^3 for clay (Miller and Gardiner, 1998). Also, bulk density is highly dependent on soil conditions at the time of sampling. Variations in soil swelling due to changes in water content alter the bulk density. Since alcohol is a polar compound, like water, its presence in the soil is likely to impact the bulk density of the soil. This may affect the fate and transport of contaminants in the soil.

2.2.3.5 Porosity (n)

Porosity is the degree to which soil contains pores through which water, air and contaminants can move. It is the volume of voids of both air and water expressed as a percentage of the total volume of a mass of soil (BS1377-1, 1990). Typical porosity values range from about 0.37 in coarse (sandy) soils to about 0.56 in fine (clayey) soils (Miller and Gardiner, 1998). Mathematically, porosity (n) is defined by Equation [2.2] (BS1377-1, 1990).

$$n = 1 - \left(\frac{\rho}{\rho_s} \right) \qquad [2.2]$$

Another expression which characterizes the amount of air in a soil is the air-filled porosity (n_a) that is defined by Equation [2.3].

$$n_a = \frac{\text{volume of air}}{\text{volume of soil}} = n - \theta_v \qquad [2.3]$$

where θ_v is the volumetric water content of a soil defined in Section 2.2.3.6.

2.2.3.6 Soil water content (θ)

The soil water content is the mass of water which can be removed from the soil, usually by heating at 105^o C, expressed as a percentage of the dry mass (BS1377-1, 1990). According to Yong (2001), any increase or decrease in soil water content changes the mechanical and physical properties of the soil. As established by Steinberg and Kreamer (1993), even a small addition of water (1.5 – 15%) can drastically reduce the sorption of nonhydrogen-bonding volatile organic compounds by the soil. The researchers explained that the effect of the additional water is to simply reduce the available surface area of the soil by filling of the soil pores. This results in the blockage of the high-energy sorption sites and thus a substantial reduction in the surface activities of the soil. Similarly, Serrano and Gallego (2006), in their sorption study with 25 volatile organic compounds, noted that the presence of water reduced the sorption of the organic compounds by occupying the active sites of the tested soils thereby reducing the amount of these sites for interactions with organic compounds. Acher et al. (1989) found that the increase in the water content of a soil resulted in a drastic decrease in the adsorption of the vapour components of a synthetic kerosene. Smith et al. (1990) noted that the sorption of trichloroethene decreased with increasing soil moisture content. Johnson and Perrott (1991) in their study on the gasoline vapour transport through a high-water-content soil found that gasoline vapours transport was quite slow. Site (2001) reported that the adsorption of neutral organic contaminants by soil mineral fraction was insignificant in wet soils due to the strong dipole interaction between soil minerals and

water, which excludes the contaminants from such portion of the soil. According to Ong and Lion (1991), increasing the water content of soils covers the hydrophilic moieties with water leaving only the more hydrophobic regions for the sorption of contaminants. Consequently, lower K_d values were reported for trichloroethylene with increasing soil water content (Ong and Lion, 1991). This indicates that fuel-alcohols can significantly affect the sorption capacities of wet soils.

Soil water content can be defined on either mass or volume basis (Sumner, 2000). Soil water content on mass basis (θ_m or gravimetric) is expressed relative to the mass of oven dry soil in Equation [2.4].

$$\theta_m = \frac{\text{mass of water}}{\text{mass of dry soil}} = \frac{(\text{mass of wet soil}) - (\text{mass of oven dry soil})}{\text{mass of oven dry soil}} \quad [2.4]$$

Soil water content on volume basis (θ_v or volumetric) is defined as the volume of water per bulk volume of soil in Equation [2.5].

$$\theta_v = \frac{\text{volume of water}}{\text{bulk volume of soil}} = \frac{(\text{mass of water/density of water})}{\text{sample volume}} \quad [2.5]$$

According to Ong and Lion (1991), the moisture of the unsaturated zone may range from fairly dry at surface to saturation at the capillary fringe of the water table. And for most of the unsaturated zone, it can be assumed that soils are generally at a moisture content corresponding to their ability to retain water, called field capacity. Therefore, it is more appropriate to perform unsaturated zone study at soil water content equivalent to the field capacity.

The soil water content is determined mostly by gravimetric method because it is a direct and inexpensive method. The conventional procedure is described elsewhere (ISO11461, 2001; Liu and Evett, 2009).

2.2.3.7 Soil organic matter

Soil organic matter (SOM) is the sum of all natural and thermally altered biologically derived organic material found in the soil or on the soil surface irrespective of its source, whether it is living, dead or in a stage of decomposition, but excluding the above-ground portion of living plants (Sumner, 2000). SOM consists of three broad classes of organic material, namely (1) living plants, animals and microorganisms; (2) fragments of dead plants, animals and microorganisms; and (3) highly decomposed and chemically variable organic compounds, also known as humus that typically makes up about 60 to 80% of the total SOM (Bohn et al., 2001; Dubbin, 2001). An alternative classification splits SOM into non-humic and humic substances (Mohamed and Antia, 1998; Sparks, 2003; Yong, 2001; Yong et al., 2012). The non-humic substances persist in the soil only for a brief time, and consist of carbohydrates, proteins, peptides, amino acids, fats, waxes and low-molecular-weight acids (Mohamed and Antia, 1998; Sparks, 2003). The humic substances are the dominant components of the SOM in soils, and comprise humic acid, fulvic acid and humin, which can be separated based on their extractability in dilute base solutions and solubility in dilute acid solutions (Stevenson, 1994; Yong, 2001; Yong et al., 2012). Compared to humic acid, fulvic acid has higher contents of carboxylic and phenolic groups and higher hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) atomic ratios. Humin is less understood due to its nonextractability, but may include complex compounds ranging from unaltered or less-altered biopolymers, such as humic acid-like materials,

kerogen, lignin, mineral-bound lipids and polysaccharides (Huang et al., 2003). The decrease in aromaticity between humic aids, fulvic acids, and humins reflects the biodegradation sequence of humins, beginning with degradation of non-amorphous organics into humic acids and continuing on to fulvic acids and finally humins (Yong, 2001; Yong et al., 2012). The variation in aromaticity and related functional groups can significantly impact sorption of alcohol-blended gasoline.

A variety of surface functional groups exist in the SOM as shown in Figure 2.4 (Mohamed and Antia, 1998; Yong, 2001; Yong et al., 2012). The major SOM functional groups are derived from lignin-like compounds, proteins, and in decreasing quantities, hemicelluloses, celluloses, and ether and alcohol soluble compounds (Sparks, 2003). The basic structure of SOM is formed by carbon bonds that are combined in saturated or non-saturated rings (salicyclic or aromatic rings, respectively) or chains (Yong, 2001; Yong et al., 2012). These functional groups control most of the properties of SOM and their reactions with other materials in a soil-water system. The most common functional groups are hydroxyls, carboxyls, phenolic and amines (Mohamed and Antia, 1998; Yong, 2001; Yong et al., 2012). They all have high sorption capacity for polar compounds, such as fuel alcohols.

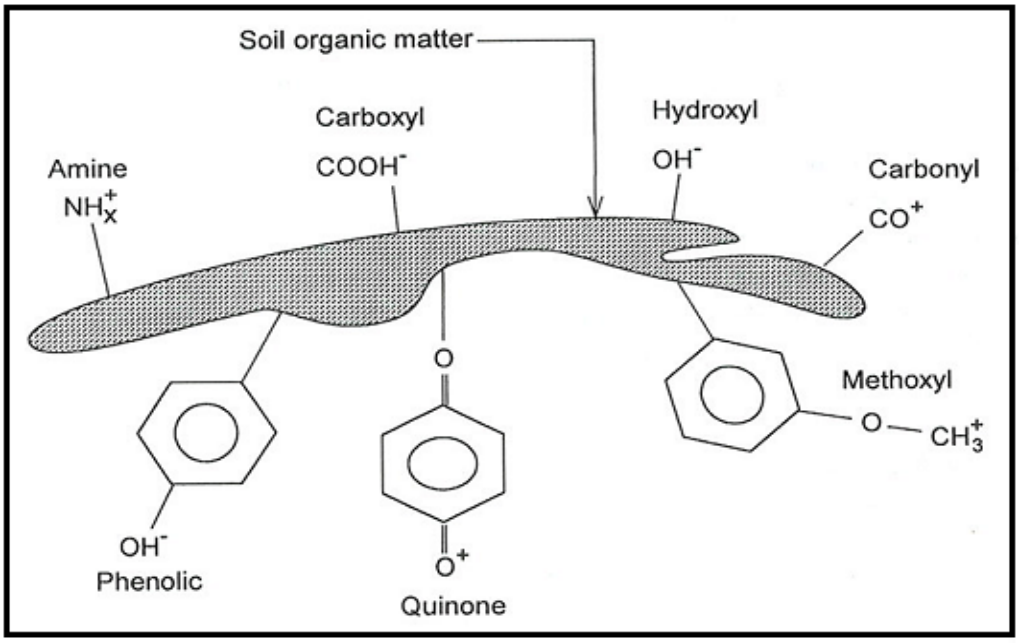

Figure 2.4 Sketch of SOM showing the various types of functional groups associated with it (Adapted from Yong, 2001).

Table 2.2 shows the reported proportions of each functional group. The reported wide ranges of values has been attributed to differences in SOM composition, such as source material, degradation and various other processes, as well as the extraction and testing procedures (Yong, 2001; Yong et al., 2012). The carboxyl group is the major contributor to the acid properties of the SOM. Carboxyls and phenolic OH groups also contribute significantly to the cation exchange capacity of the SOM, and hence, are considered to be the most important functional groups (Yong, 2001; Yong et al., 2012).

Table 2.2 Proportions of functional groups found in SOM for fulvic acid, humic acid, and humin (Adapted from Yong et al., 2012).

Functional group	Fulvic acid	Humic acid	Humin
Carbonyl, %	Up to 5	Up to about 4	NA
Carboxyl, %	1-6	3-10	NA
Quinone, %	2±	1-2	NA
Ketones, %	2±	1-4	NA
Alcoholic OH, %	2.5-4	Up to 2	NA
Phenolic OH, %	2-6	Up to about 4	NA

NA = Not applicable

In soft soils, SOM may be as high as 5% while in sandy soils the content is often less than 1% (Bohn et al., 2001; Sparks, 2003; Yong, 2001; Yong et al., 2012). Even at these low levels, the reactivity of SOM is so high that it has a pronounced effect on soil physical and chemical properties (Bohn et al., 2001; Sparks, 2003). The quantity of SOM in a soil depends on five soil-forming factors, namely time, climate, vegetation, parent material and topography. Other factors, such as cultivating soils and wetting and drying of soils, also affect the content of SOM. These factors vary for different soils. Hence, SOM accumulates at different rates and, therefore, in varying quantities (Sparks, 2003).

Studies on the sorption of contaminants by soil have shown that SOM strongly dictates soil physical and chemical properties. Thus, the SOM content of soils is the factor most directly related to the sorption of most organic compounds by soils and strongly influences organic compounds behaviour in soil, including leachability, volatility and biodegradability (Huang et al., 2003; Sparks, 2003). Hence, there is a strong need to establish how different SOM levels may affect the sorption of alcohol-blended fuels. The addition of SOM to soils has been found to enhance the

sorption of contaminants by soils (Li et al., 2009) mainly due to its high specific surface area and cation exchange capacity (Chen et al., 2007; Sparks, 2003). Although, the primary soil components responsible for sorption of contaminants is mainly SOM, clay minerals also play a role (Sparks, 1989). Joo et al. (2008) found that the overall sorption of nonpolar organic compounds is determined by sorption to both SOM and mineral surface, and the dominance of either contribution depends on the properties of the sorbents, such as surface area, pore geometry, intrinsic sorptive affinity of mineral surface and the properties of the organic compound, including hydrophobicity and solubility. In addition, it has been suggested that the impact of SOM on the sorption of contaminants would vary for different compounds (Shi et al., 2010; Wang et al., 2008a) and for different soils (Serrano and Gallego, 2006) due to the different types of SOM contained in different soils that exhibit capacity limiting sorption processes (Huang et al., 2003).

As established by Weber et al. (1992), there are two types of physically and chemically different SOM, namely soft carbon, also called amorphous SOM phase, such as humic matter, and hard carbon that is a relatively condensed SOM phase. Sorption of hydrophobic organic compounds, such as gasoline compounds, into the soft carbon SOM phase will follow a virtually linear partitioning process whereas sorption on the hard carbon SOM phase will exhibit both adsorption and absorption or partitioning (Weber et al., 1992). Therefore, depending on the relative contents of the two SOM phases in the soil, sorption of hydrophobic organic compounds by soils could range from linear partitioning to highly nonlinear adsorption (Huang and Weber, 1997). More so, Huang and Weber (1997) have noted that SOM differs in oxygen-to-carbon atomic ratio (O/C) and that a decrease in the O/C of an SOM increases its hydrophobicity and driving

force (hydrophobic interaction) for sorption. The main constituents of SOM are Carbon (52-58%), Oxygen (34-39%), Hydrogen (3.3-4.8%), and Nitrogen (3.7-4.1%) (Sparks, 2003). According to Huang et al. (2003), the rates and equilibria of sorption and desorption correlate well with the types of SOM and their physicochemical properties. More so, a number of studies have indicated that varied sorption phenomena, such as isotherm nonlinearity, varied sorption capacity, sorption-desorption hysteresis and slow rate of sorption and desorption, relate primarily to the diverse nature of SOM, which can be found by laboratory measurements (Allen-King et al., 2002; Celis et al., 2006; Huang and Weber, 1997; Karapanagioti et al., 2001; Lueking et al., 2000).

The laboratory measurement of SOM can be carried out using wet chemical oxidation method, automated dry combustion method or loss-on-ignition method (Konen et al., 2002). However, because wet chemical oxidation method requires the use of hazardous material, such as concentrated H_2SO_4, and automated dry combustion equipment is expensive and can require time-consuming maintenance, they are sparingly used in the laboratory for the determination of SOM (Konen et al., 2002). On the other hand, loss-on-ignition method requires only muffle furnace, drying oven and balance, all of which are readily available in most laboratories and relatively inexpensive to purchase, operate and maintain (Konen et al., 2002).

2.2.4 Properties of contaminants that affect their fate and transport

There are several properties of contaminants that largely determine their fate and transport in the subsurface environment. These properties include

density, viscosity, solubility, vapour pressure, volatility, interfacial tension, wettability and octanol-water partition coefficient. They have been related to alcohol-blended fuels as below.

2.2.4.1 Density

The density of a substance is the ratio of its mass to its volume and varies with molecular weight, interaction and structure (Lyman et al., 1990), and may also vary with temperature and pressure (Bear, 1972). In environmental investigation, the density of a substance is used to determine its likely migration pattern. Density is often presented in terms of specific gravity, which is the density of a substance to the density of a standard, usually water for a liquid or solid, and air for a gas. At normal temperatures and pressures, the typical density range are 0.6 to 2.9 g/mL for liquids, 0.97 to 2.7 g/cm^3 for solids and 0.5 to 3.0 g/L for gases (Lyman et al., 1990). As reported by Mercer and Cohen (1990), gasoline densities differ from water by 10 - 50% in many situations, and a density difference of about 1% could influence fluid movement in the subsurface. Since ethanol and n-butanol have densities of 0.789 and 0.839 g/mL respectively, compared to 0.71 – 0.77 g/mL for gasoline, this could have a significant effect on alcohol-blended gasoline during spill (Fetter, 1999; Huling and Weaver, 1991; Mercer and Cohen, 1990).

2.2.4.2 Viscosity

The viscosity of a fluid is the internal friction derived from internal cohesion within the fluid that causes it to resist flow and is vital for predicting the movement of bulk quantities of fluids. For instance, knowledge of the viscosity is required in formulas relating to the flow rate (e.g. from tank),

or spreading (e.g. on water) during a chemical spill. As the temperature of a fluid increases, the cohesive forces decrease and the absolute viscosity decreases. Values of viscosity for organic liquids generally range from 0.3 to 20 cp at ambient temperatures, while water has a viscosity of 1 cp at 20 ^{o}C (Lyman et al., 1990). Among the alcohols, viscosity increases with increasing carbon chains. Hence, butanol has a higher viscosity of 3.0 cp than ethanol of 1.19 cp. The lower the viscosity, the more readily a fluid will penetrate a porous medium (Huling and Weaver, 1991). Therefore, the addition of ethanol to gasoline is likely to cause greater transport of the gasoline compounds in the subsurface environment than the addition of butanol. For a fluid consisting of a mixture of light and heavy compounds, such as alcohol-blended gasoline, the viscosity may change with time as a result of gradual loss of the light group from the mixture (Mercer and Cohen, 1990). An important term relating to viscosity is the mobility ratio given by the gasoline-water viscosity ratio. According to Mercer and Cohen (1990), a mobility ratio >1, e.g. butanol and benzene, favour the flow of water whereas those <1, e.g. benzene only, favour the flow of gasoline.

2.2.4.3 Solubility

The aqueous solubility of a compound is the maximum amount of the compound that will dissolve in pure water at a particular temperature (Lyman et al., 1990). The solubility of compounds varies greatly in particular when mixing polar compounds with non-polar, such as in alcohol-blended gasoline. The non-polar hydrophobic compounds, such as gasoline compounds, are less soluble than the polar hydrophilic compounds, such as alcohols. The highly soluble compounds tend to have relatively low adsorption coefficients in soils and also tend to be more readily biodegradable by microorganisms (Lyman et al., 1990). Other degradation

pathways (e.g. hydrolysis and oxidation) and specialised transport pathways (e.g. volatilization and leaching) are also affected by the extent of water solubility. The solubilities of most common organic compounds are in the range of 1 to 100,000 ppm at ambient temperatures. However, several are higher and some are infinitely soluble and are miscible with water in all proportions (Lyman et al., 1990). For example, the solubility of butanol is about 80, 610 ppm compared to ethanol that is infinitely soluble. On the other hand, isooctane, a good representative of gasoline compounds, is insoluble in water. This suggests that the solubility of ethanol-blended gasoline is likely to be higher than that of butanol-blended gasoline. Factors that affect the solubility of compounds include temperature, salinity, cosolvents, dissolved organic matter and pH. Most organic compounds become more soluble as the temperature increases, but some behave in the opposite way. The presence of dissolved salts or minerals in water leads to moderate decreases in solubility, while the presence of dissolved organic material, such as naturally occurring humic and fulvic acids, enhances the aqueous solubility of many organic compounds. In general, the aqueous solubility of compounds decreases with increasing molecular weight and structural complexity (Huling and Weaver, 1991). For a contaminant, such as gasoline that comprises a mixture of range of compounds, solubility will lead to the rapid loss of the more soluble compounds, leaving behind the less soluble compounds. Blending gasoline with alcohol can significantly alter this process. This results in changes to the ratios of compounds in the nonaqueous phase liquid (NAPL) and dissolved plume with time that may affect the vapour pressure (Lyman et al., 1990; Mercer and Cohen, 1990).

2.2.4.4 Vapour pressure

The vapour pressure of a compound determines how readily vapours volatilise from the pure liquid phase (Fetter, 1999; Lyman et al., 1990). It is generally reported as the pressure of the gas in equilibrium with the liquid at a given temperature (Hemond and Fechner-Levy, 2000; Munowitz, 2000; Schwarzenbach et al., 1993). Vapour pressure is a vital tool in predicting the behaviour and fate of chemicals that are introduced into the environment (Lyman et al., 1990; Schwarzenbach et al., 1993), since the persistence of chemicals that have been absorbed in the soil is highly dependent on vapour pressure (Lyman et al., 1990). For example, when a chemical has been spilled, knowledge of the vapour pressure of the chemical is crucial in order to estimate its rate of evaporation or volatility. Considering the discrepancy in the vapour pressure of isooctane (5500 Pa), ethanol (5950 Pa) and butanol (500 Pa), it is likely that the addition of either ethanol or butanol to isooctane will impact the vapour pressure of the resulting blend. More so, the difference in vapour pressure between ethanol and butanol may result in different behaviour of the resulting blends in the vadose zone and the overall impact of a spill.

For a mixture of volatile compounds, such as in gasoline, the vapour pressure of the individual compounds in the liquid solution is described by Raoult's law. This law applies to ideal solutions and states that the vapour pressure of each volatile compound is proportional to its mole fraction in solution (Brady et al., 2000; Munowitz, 2000; Oxtoby et al., 2012). The total vapour pressure of the solution is expressed by the Dalton's law of partial pressures as the sum of the partial pressures exerted by each volatile compound (Brady et al., 2000).

$$P_i = X_i P_i^o \qquad \text{(Raoult's law)}$$

$$P_{total} = X_1 P_1^o + X_2 P_2^o + X_3 P_3^o + ... + X_n P_n^o \qquad \text{(Dalton's law)}$$

where P_i is the vapour pressure of the component i in the solution, X_i is the mole fraction of the component i in the solution, and P_i^o is the vapour pressure of the pure component i.

Nonideal solutions may show either higher (positive) or lower (negative) deviation from the vapour pressure predicted by Raoult's law (Brady et al., 2000; Munowitz, 2000; Oxtoby et al., 2012). According to Munowitz (2000), ideality for a solution implies total uniformity of interaction. Although real solutions are rarely ideal (Brady et al., 2000), at a low concentration, as used in this study, a solution of volatile liquids could be considered ideal (Munowitz, 2000). For such an ideal solution, the vapour pressure of each component could be used as the expression of the partial pressure of the component in the gas phase in equilibrium with the liquid phase, and can be converted to gas phase concentration using the ideal gas law (Hemond and Fechner-Levy, 2000; Vallero, 2004).

$$\frac{n}{V} = \frac{P_i}{RT} \qquad \text{(Gas phase concentration)}$$

where V is the volume of the container, n is the number of moles of chemical, and R is the universal gas constant.

The vapour pressure of contaminants affects their partitioning and volatilization rates and has been used to categorize contaminants into

volatile, semivolatile and nonvolatile. Contaminants with vapour pressure values greater than 10^{-2} kPa are termed volatile while those with vapour pressure values between 10^{-5} and 10^{-2} kPa and less than 10^{-5} kPa are classified as semivolatile and nonvolatile, respectively (Vallero, 2004). Volatile contaminants, such as gasoline compounds, form higher concentrations of vapour above the liquid and are potential air pollutants. When released from leaking underground storage tank, the vapour pressure of volatile contaminants could lead to their upward transport in the vapour phase as shown earlier in Figure 2.3 in Section 2.2.1.1. A review of the transport of volatile organic contaminants in the environment has revealed that vapour pressure is a key property that controls the transport rate of organic contaminants (Mackay and Wania, 1995). In addition, the study on the volatilization of gasoline from soil found that the volatilization rate of the gasoline compounds increased with increasing vapour pressure (Arthurs et al., 1995).

Since the vapour properties of a solution depends on the number of its components (Munowitz, 2000; Oxtoby et al., 2012), the addition of an extra compound to a gasoline mixture may possibly impact the vapour pressure of the individual gasoline compounds in the mixture due to change in mole fraction. Thus, the addition of either ethanol or butanol to gasoline may change the vapour pressure of the gasoline compounds. Knowing the extent of this change would be important in predicting the fate and transport of alcohol-blended gasoline vapours in the vadose zone.

2.2.4.5 Volatility

The volatility of a compound is the measure of the transfer of the compound from the aqueous phase to the vapour phase (Lyman et al., 1990). Knowledge of volatilization rates is necessary to determine the amount of a contaminant that enters the gas phase and the change of the contaminant concentrations in soils and water bodies. In the case of spills or purposeful application of a chemical to the soil, the period of time the chemical persist in the soil is determined to a large extent by the rate of volatilization of the chemical. The rate at which a chemical volatilizes from soil is affected by its chemical properties, the soil properties and surrounding conditions. Some of the chemical properties involved during volatilization include vapour pressure, aqueous solubility, molecular weight and molecular structure. The soil and environmental properties that affect the volatilization rate of a contaminant are its concentration in the soil, the soil water content, the airflow rate over the surface, humidity, temperature, sorption and diffusion characteristics of the soil, bulk properties of the soil, such as organic matter content, porosity, density and clay content. All of these factors affect the distribution of a compound between the soil solid, soil water and soil air phases (Lyman et al., 1990). The Henry's law constant (H), expressed as the ratio of a contaminant's concentration in air to its concentration in water at equilibrium, is a valuable parameter for estimating the tendency of a compound to volatilize from aqueous phase (Hemond and Fechner-Levy, 2000; Vallero, 2004). The greater the H of a compound, the greater the tendency to volatilize from the aqueous phase (Huling and Weaver, 1991). The H values for butanol ($4.99*10^{-4}$) and ethanol ($2.94*10^{-4}$) are significantly lower than that for isooctane (132.4) (Yaws, 2008). Thus, the addition of butanol or ethanol to gasoline is likely to affect the volatility of the resulting fuel. Also, since the value of H gives an indication of hydrophobicity, the difference in

H between alcohol and isooctane may result in change in the interfacial tension for alcohol-blended gasoline in the vadose zone compared with alcohol-free gasoline.

2.2.4.6 Interfacial tension

Interfacial tension is the surface energy at the interface between two liquids that results from differences in the forces of molecular attraction within the fluids and at the interface (Bear, 1972). The interfacial tension between an organic liquid and water affects processes such as the formation of stable emulsions, the resistance to flow through pores and the dispersion of droplets (Lyman et al., 1990). The knowledge of interfacial tension may be important when attempting to determine the fate of a chemical of environmental concern or when removing a toxic compound from an aqueous environment. Interfacial tension is directly related to the capillary pressure across an NAPL-water interface and is a factor controlling wettability. It decreases with increasing temperature and may be affected by pH, surface-active agents and gas in solution (Mercer and Cohen, 1990). The interfacial tensions of NAPL-water range from zero, for completely miscible liquids, to 72 dynes/cm at 25 ^{o}C (Lyman et al., 1990). Since ethanol and butanol are significantly more soluble than isooctane (see Section 2.2.4.3), the addition of any of the alcohols to gasoline may reduce the interfacial tension of the resulting alcohol-blended gasoline and, hence, may increase the wettability of the gasoline.

2.2.4.7 Wettability

Wettability refers to the preferential spreading of a fluid over a solid surface in a two-phase system. A measure of wettability is the contact

angle (Ø) at the fluid-solid interface as shown in Figure 2.5. A fluid is considered a wetting fluid if Ø<90^o and a non-wetting fluid if Ø>90^o. A wetting fluid will tend to occupy the smaller pore spaces, while a non-wetting fluid will tend to be restricted to the largest interconnected pore spaces (Mercer and Cohen, 1990). The Ø values for individual organic compounds are scarce in the literature. However, polar compounds generally have higher wettability or lower Ø, while non-polar compounds have lower wettability or higher Ø (Crocker and Marchin, 1988). As reported by Huling and Weaver (1991), contact angle is an indicator used to determine whether porous material will be preferentially wetted by either the NAPL or the aqueous phase. For two fluids, such as NAPL and water, in contact with a solid, the contact angle is given by Equation [2.6] (Mercer and Cohen, 1990).

$$\text{Cos}\,\phi = \frac{\sigma_{Ns} - \sigma_{ws}}{\sigma_{Nw}} \qquad [2.6]$$

where σ_{Ns} is the interfacial tension between NAPL and solid, σ_{ws} is the interfacial tension between water and solid, and σ_{Nw} is the interfacial tension between NAPL and water.

According to Mercer and Cohen (1990), wettability relations in NAPL-water systems are affected by the medium mineralogy, NAPL chemistry, water chemistry, presence of surfactants or organic matter and medium saturation history. Although water is often the wetting fluid in NAPL-water systems, NAPL wetting usually increases due to adsorption and/or deposition on mineral surfaces of organic matter and the presence of surfactants. NAPL wetting has been reported to increase with time during contact angle studies, presumably due to mineral surface chemistry

modifications induced by NAPL presence that might change the solubility in water (Mercer and Cohen, 1990).

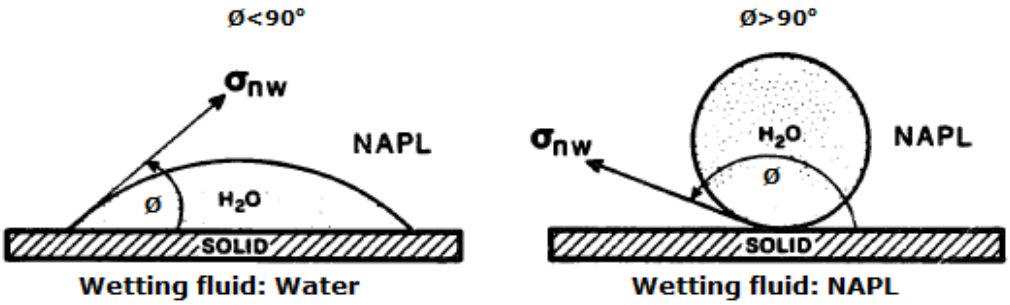

Figure 2.5 Contact angle in NAPL-water systems (Modified from Mercer and Cohen, 1990).

2.2.4.8 Octanol-water partition coefficient

The octanol-water partition coefficient (K_{ow}) is a measure of the degree to which an organic compound will preferentially dissolve in water or an organic solvent (Lyman et al., 1990). The coefficient is the ratio of the equilibrium concentration of the compound in octanol ($C_{octanol}$) to the equilibrium concentration in water (C_{water}) as shown in Equation [2.7] (Fetter, 1999; Lyman et al., 1990).

$$K_{ow} = \frac{C_{octanol}}{C_{water}} \qquad [2.7]$$

The greater the K_{ow} value, the greater the tendency to partition to the organic phase, such as the SOM, rather than to the water, and the less mobile the compound tends to be in the environment (Fetter, 1999). Soils with low SOM content can retain organic compounds with high K_{ow} values, but might not retain those with low K_{ow} values (Fetter, 1999). Hence, K_{ow} is a key parameter in the study of the environmental fate of organic

compounds and has been found to be related to water solubility and soil adsorption (Lyman et al., 1990). Any organic compound with K_{ow} <10 is considered hydrophilic and tends to have high water solubility and small soil adsorption, while an organic compound with K_{ow} >1*10^4 is very hydrophobic (Lyman et al., 1990). Accordingly, ethanol and butanol with K_{ow} values of 0.50 and 6.92, respectively, are hydrophilic while isooctane with a K_{ow} value of 1.23*10^4 is hydrophobic. Therefore, blending a gasoline with any of the alcohols may affect the adsorption of the gasoline compounds of the resulting blends in the vadose zone after a spill. Thus, it is important to know the degree of this impact for the different alcohols as they are used as gasoline oxygenates.

2.2.5 Summary of contaminant properties related to this study

Table 2.3 summarizes the properties and the threshold and permissible exposure limits for the gasoline compounds used in this research. With the exception of the biodegradability of contaminant which was not considered in this work, the properties of contaminants most relevant to their fate and transport in the subsurface environment are vapour pressure and solubility (both individually and as they relate to Henry's law constant) and sorption which is represented by octanol-water partition coefficient (ITRC, 2005). The gasoline compounds are highly hydrophobic with lower water solubility and higher octanol-water partition coefficient and Henry's law constant than the alcohols. Consequently, while the gasoline compounds would partition from the gas phase to the soil solid phase, the alcohols would tend to partition from the gas phase into the soil water phase. The vapour pressure of the gasoline compounds ranged from 57,900 Pa for pentane to 1,470 Pa for octane. Ethanol and butanol, on the other hand, have vapour

pressure of 5,950 Pa and 500 Pa, respectively. Unlike butanol, ethanol has higher vapour pressure than most gasoline compounds and therefore would volatilize more readily from light, nonaqueous-phase liquid (ITRC, 2005; USEPA, 2005). Hence, according to Reynolds (2002), when ethanol is added to gasoline, the resulting fuel would have a higher vapour pressure than the unblended gasoline. As alcohols, ethanol and butanol are miscible with water and other organic solvents, such as gasoline (Niven, 2005; Powers et al., 2001b; Zhang et al., 2006). However, ethanol has higher miscibility with water, less miscibility with gasoline (USEPA, 2005). Butanol is more effective for water solubility in blends than ethanol (USEPA, 2005). In addition, butanol has less phase separation problem and is far less corrosive than ethanol, therefore, can be distributed through existing gasoline pipelines (EBTP, 2009).

The alcohols have very low Henry's law constant indicating that the impact of solubility would far exceed that of vapour pressure (ITRC, 2005). A comparison of the solubility and vapour pressure values for the alcohols and the gasoline compounds upholds this claim. For example, while the vapour pressure of the most volatile gasoline compound (pentane) is about 116 times that of the least volatile alcohol (butanol), the solubility of butanol is about 2015 times that of pentane. Therefore, the blending of gasoline with any of the alcohols is likely to have greater impact on the solubility than on the vapour pressure of the gasoline compounds.

Like the vapour pressure, the relative solubility of each gasoline compound in gasoline mixture is defined by Raoult's law as the product of the compound's pure phase solubility and its mole fraction in the gasoline mixture (ITRC, 2005). Since the vapour pressure and solubility of individual gasoline compounds in gasoline mixture depends on the number of the

gasoline components (ITRC, 2005; Munowitz, 2000; Oxtoby et al., 2012), the addition of an extra compound to a gasoline mixture may possibly impact the vapour pressure and solubility of the individual gasoline compounds in the mixture due to change in mole fraction. More so, based on the differences in the solubility and vapour pressure of the gasoline compounds and the alcohols, it is likely that the presence of alcohol will affect the adsorption and vapour phase transport of petroleum soil and groundwater contaminants following release to the vadose zone. Understanding the extent of these effects for ethanol and butanol would be critical to the development of appropriate management plan for sites contaminated with ethanol or butanol blended fuels.

Table 2.3 Summary of properties of synthetic fuel compounds as well as threshold and permissible exposure limits.

Fuel compound	**Formula**	**MW (g/mol)**	**Density at 25°C (g/mL)**[a]	**Boiling point (°C)**[a]	**VP at 20°C (Pa)**[a]	**Solubility at 25°C (g/L)**[c]	**Log K_{oc}**[c]	**Log K_{ow}**[c]	**H**[d]	**TLV (mg/L)**[c]	**PEL (mg/L)**[c]
Pentane	C_5H_{12}	72	0.626	35.5	57900	0.04	3.25	3.45	51.4	600	1000
Octane	C_8H_{18}	114	0.703	126	1470	0.0004	4.18	5.15	211	300	500
MCP	C_6H_{12}	84	0.75	72	17732[b]	0.04	3.21	3.37	14.7	-	-
MCH	C_7H_{14}	98	0.77	101	4930	0.01	3.49	3.88	17.5	400	500
Benzene	C_6H_6	78	0.874	80	9950	1.76	1.87	2.13	2.26E-01	0.5	1
Toluene	C_7H_8	92	0.865	110.5	2910	0.54	1.97	2.73	2.65E-01	50	200
Fuel additive											
Ethanol	C_2H_5OH	46	0.789	78	5950	Total	1.21	-0.30	2.94E-04	1000	1000
Butanol	C_4H_9OH	74	0.811	117.7	500	80.61	1.83	0.84	4.99E-04	-	100

[a] values obtained from Sigma Aldrich MSDS (Material Safety Data Sheet); [b] value obtained from Pasteris et al. (2002) Supporting Information; [c] obtained from Yaws (2008); [d] converted values from Yaws (2008); MCP – Methylcyclopentane; MCH – Methylcyclohexane; MW – Molecular weight; VP – Vapour Pressure; K_{oc} – Soil sorption coefficient; K_{ow} – Octanol-Water partition coefficient; H – Henry's Law Constant; TLV – Threshold Limit Value; PEL – Permissible Exposure Limit.

2.3 Soil and groundwater contaminants

Studies on the contamination of soil and groundwater have identified a wide variety of substances as soil and groundwater contaminants including organics, metals and non-metals, pathogens and radionuclides (Fetter, 1999). This study focuses on the organic contaminants from a spill, including general hydrocarbons, petroleum specific and alcohols.

2.3.1 Hydrocarbons

Hydrocarbons are composed of carbon and hydrogen and are used extensively in fuels, paints, paint and spot removers, dry cleaning solutions, lamp oil, lubricants, rubber cement and solvents. Hydrocarbons can be classified as being paraffinic, such as pentane and octane, naphthenic, including cyclopentane and cyclohexane, and aromatic, such as benzene and toluene (Fetter, 1999; Levine, 2011). The physical and chemical differences between these classes of hydrocarbons are summarised in Table 2.3 in Section 2.2.5. Generally, the aromatics are less hydrophobic than the paraffins and naphthenes. Hence, they partition more to the soil water after release. Consequently, the aromatics are more likely to be transported via the dissolved phase than the paraffins and naphthenes after a spill or leak into the vadose zone.

2.3.2 Petroleum hydrocarbons

Petroleum hydrocarbons are hydrocarbons derived from petroleum, a naturally occurring, flammable liquid found in rock formations in the earth (Levine, 2011; Speight, 2002). Petroleum-derived hydrocarbons include asphalt, diesel, kerosene, gasoline, liquefied petroleum gas, lubricating

oils, paraffin wax and petrochemicals. The length of the hydrocarbon chains and degree of branching determine their phase at room temperature. While most are liquid at room temperature, for example gasoline, kerosene and diesel, some are in gas form, for example liquefied petroleum gas, and others are solid, for example asphalts and waxes (Levine, 2011). Petroleum hydrocarbons, especially gasoline are of particular concern due to contamination of soil and groundwater via spills, leaks or improper disposal. A typical gasoline contains over 150 different chemicals, including benzene, toluene, ethylbenzene and xylene known as the BTEX compounds, and some are listed in Table 2.4 (Chen et al., 2008; Hancock, 1985). The adverse health effects associated with the exposure of gasoline are strongly linked to the presence of the BTEX compounds. Exposure to small amount of gasoline could lead to nose and throat irritation, headaches, dizziness, nausea, vomiting and breathing difficulties (USEPA, 2011b). Conversely, exposure to significant amount could lead to coma or death. Also, at level above the maximum contaminant level as stipulated by the Environmental Protection Agency, some of the compounds in gasoline, for example benzene, are known to cause diseases, such as anaemia and cancer (USEPA, 2011b). Therefore, during spills it is important to predict their movements, especially when mixed with alcohols.

Table 2.4 Gasoline components (Adapted from Hancock, 1985).

Hydrocarbon family	**Paraffin (Alkane)**	**Olefin**	**Naphthene (Cycloalkane)**	**Aromatic**
Family members	Butane	Butene	Cyclopentane	Benzene
	Pentane	Pentene	Methylcyclopentane	Toluene
	Hexane	Hexene	Cyclohexane	Xylenes
	Heptane	Heptene	Methylcyclohexane	Ethylbenzene
	Octane	Octene	Higher naphthenes	C_9 aromatics
	Nonane	Nonene		
	Higher paraffins	Higher olefins		

2.3.3 Alcohols

Alcohols are added to gasoline to improve the quality and to supplement the supply of gasoline (Hancock, 1985). They may also be required for marketing or legal reasons (Owen, 1989). Presently, ethanol is the alcohol used in gasoline blending and functions as oxygenate as well as an extender. However, there are logistic challenges associated with the use of ethanol (Dakhel et al., 2003; Pasteris et al., 2002; Ulrich, 1999). Although ethanol is renewable and easily degradable under both aerobic and anaerobic conditions (Alvarez et al., 2001; Dakhel et al., 2003; Niven, 2005; Powers et al., 2001b; Ulrich, 1999; Zhang et al., 2006) and will cause minimum groundwater contamination risks on its own after accidental spills (Dakhel et al., 2003; Niven, 2005; Zhang et al., 2006), it also has its own issues. Firstly, the high possibility of phase separation of ethanol-blended gasoline prevents its preparation at a refinery and distribution by pipelines (French and Malone, 2005; Powers et al., 2001a). Consequently, gasoline distribution terminals receive gasoline and ethanol separately to be mixed and pumped into a tanker for delivery to a gasoline

station as shown in Figure 2.6. Ethanol is also more corrosive than gasoline and hence material compatibility are usually considered when designing large-volume, bulk-alcohol storage tanks (Rice, 1999).

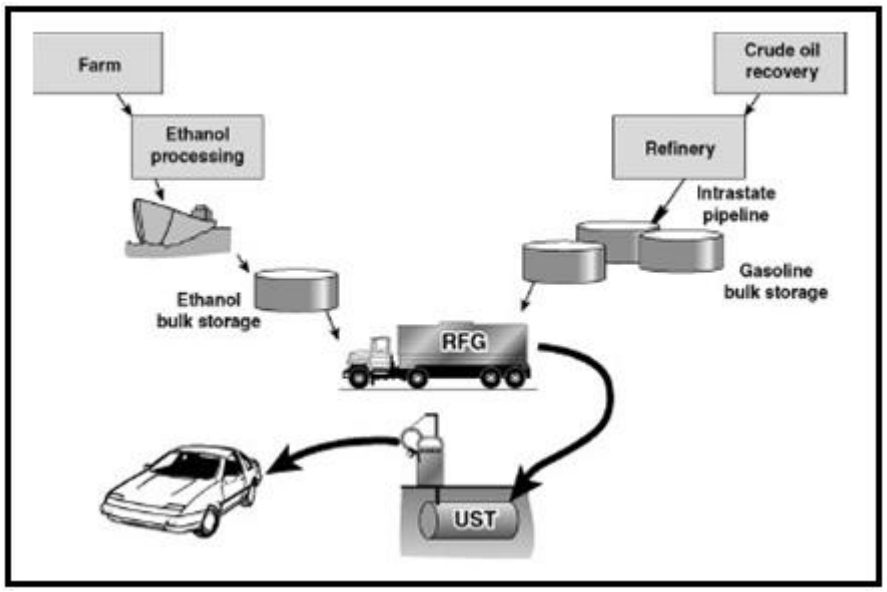

Figure 2.6 Ethanol-gasoline blending processes (Adapted from Powers et al., 2001a).

Figure 2.7 shows the phase separation of ethanol-gasoline blends in the presence of water using a ternary phase diagram. The diagram illustrates the general equilibrium phase behaviour that is expected to govern ethanol-gasoline blends phase behaviour in a subsurface environment. The shaded region represents the region where the three components exist as two separate phases, while the unshaded region represents the region where the three components exist as a single phase. The curve separating the two regions is called the binodal curve. The ends of the tie lines indicate the composition of each phase at equilibrium. The downward slope (left to right) of the tie lines indicates the preferential partitioning of ethanol into water. The effect of the fluid interactions of this ternary mixture is of fundamental importance on the understanding of the flow

behaviour of ethanol-gasoline blends in the subsurface environment after an accidental spill. Secondly, it is believed that the use of ethanol as gasoline oxygenate will increase the gasoline compounds downward migration and compete with their adsorption and biodegradation (Powers and Heermann, 1999). Recent studies have suggested that these effects would be particularly significant for ethanol concentrations higher than 10% (Adam et al., 2002; Chen et al., 2008; Corseuil et al., 2004; Dakhel et al., 2003; Reckhorn et al., 2001).

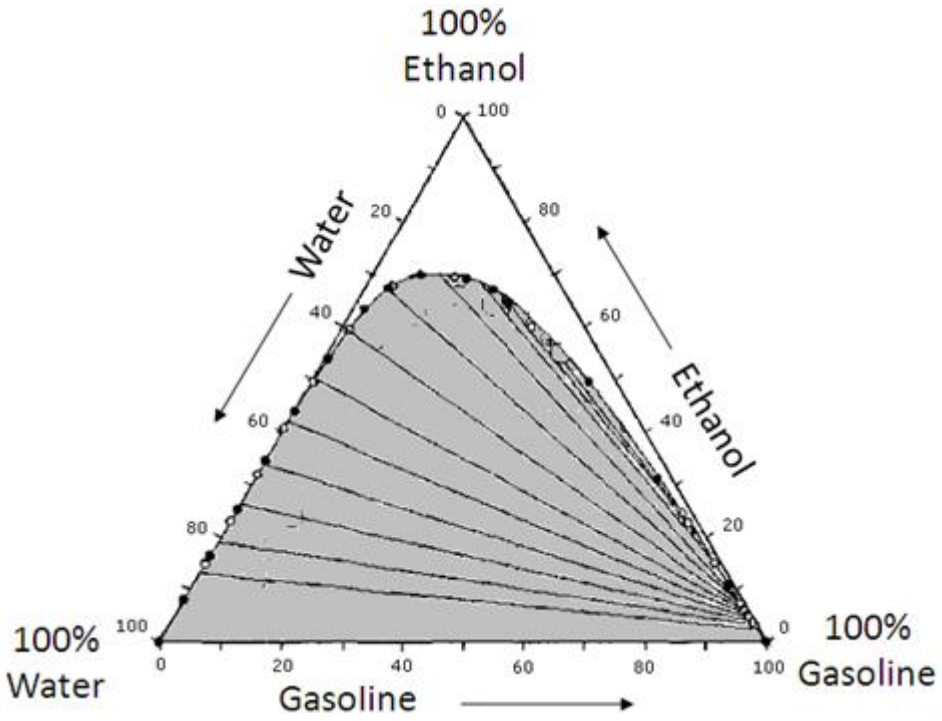

Figure 2.7 Ternary phase diagram for gasoline-ethanol-water system (Adapted from de Oliviera, 1997).

Although butanol has not historically been an attractive choice as a gasoline oxygenate due to its higher cost of production compared to ethanol, it has recently gained renewed interest. This follows some promising development associated with its production from renewable and cost-effective cellulosic materials that have the potential to reduce its

production costs (Kumar and Gayen, 2011). Also, it has several advantages over ethanol as a fuel including higher energy content, higher miscibility with gasoline, lower vapour pressure, lower water absorption, and higher compatibility with existing gasoline pipelines than ethanol (EBTP, 2009; USEPA, 2005).

2.3.4 Comparison of alcohol with gasoline

A comparison of the common properties of gasoline and alcohol fuels was made by Wallner (2011) and shown in Table 2.5. Alcohol and gasoline are both lighter than water hence when released rapidly in bulk onto water, tends to remain on the surface of the water (Rice, 1999). However, alcohol is very hydrophilic whereas gasoline is hydrophobic (Powers et al., 2001b; UTTU, 2003). Pure alcohol is poisonous, but less acutely toxic than the BTEX components in gasoline, and is heavier than unblended gasoline. Both alcohol and gasoline are very volatile and evaporate into air rapidly. Similar to gasoline vapours, alcohol vapours are denser than air and tend to settle near the ground in low areas. When burned, alcohol releases less heat than gasoline. According to Rice (1999), one and a half gallons of ethanol have approximately the same fuel combustion energy as one gallon of gasoline. Because alcohol is a metabolic by-product, many organisms tolerate concentrations that may be encountered during accidental releases into the environment (Dagley, 1984). A range of indigenous microorganisms within the environment are capable of using alcohol as an energy source and will preferentially utilize alcohol over the gasoline hydrocarbons (Alvarez and Hunt, 1999).

Table 2.5 Comparison of gasoline and alcohol fuel properties (Adapted from Wallner, 2011).

Property	**Gasoline**	**Alcohol**	
		Ethanol	**n-Butanol**
Chemical formula	C_4-C_{12}	C_2H_5OH	C_4H_9OH
Composition (C,H,O) (% mass)	86,14,0	52,13,35	65,13.5,21.5
Lower heating value (mJ/kg)	42.7	26.8	33.1
Density (kg/m^3)	715-765	790	810
Octane number ((R+M)/2)	90	100	87
Boiling temperature (^{o}C)	25-215	78	117
Latent heat of vaporization at 25^{o}C (kJ/kg)	380-500	919	706
Self-ignition temperature (^{o}C)	~300	420	343
Stoichiometric air/fuel ratio	14.7	9.0	11.2
Laminar flame speed (cm/s)	~33	~39	-
Mixture calorific value (mJ/m^3)	3.75	3.85	3.82
Lower ignition limit in air (vol %)	0.6	3.5	1.4
Upper ignition limit in air (vol %)	8	15	11.2
Solubility in water at 20^{o}C (mL/100 mL H_2O)	<0.1	Fully miscible	7.7

2.3.5 Possible health risks of alcohol in gasoline

Direct effects of alcohol in gasoline would appear to be minimal even in cases of severe contamination, although the adverse consequences of contamination by the hydrocarbon fraction of the gasoline would remain (Rice and Cannon, 1999). However, the indirect effects of alcohol, such as enhancement of migration through soil and inhibition of biodegradation of gasoline compounds, could increase the concentrations of the toxic gasoline compounds (BTEX compounds) in groundwater (Adam et al., 2002; Alvarez et al., 2001; Corseuil et al., 1998; Mackay et al., 2006; McDowell and Powers, 2003; Österreicher-Cunha et al., 2007; Österreicher-Cunha et al., 2009; Reckhorn et al., 2001). Thus, alcohol in

gasoline is believed to result to more exposure to human carcinogen, such as benzene, and non-carcinogens, such as toluene and xylenes, for which some adverse health effects might be anticipated from the soil and groundwater contamination (OEHHA, 1999).

2.4 Fate of contaminants in the subsurface environment

The subsurface environment is divided into two major zones, namely unsaturated and saturated zones as shown in Figure 2.8. The texture of the porous material forming the unsaturated and saturated zones may range from coarse sand, through finer-textured silt, to extremely fine-textured clay as explained in Section 2.2.2 (Hemond and Fechner-Levy, 2000).

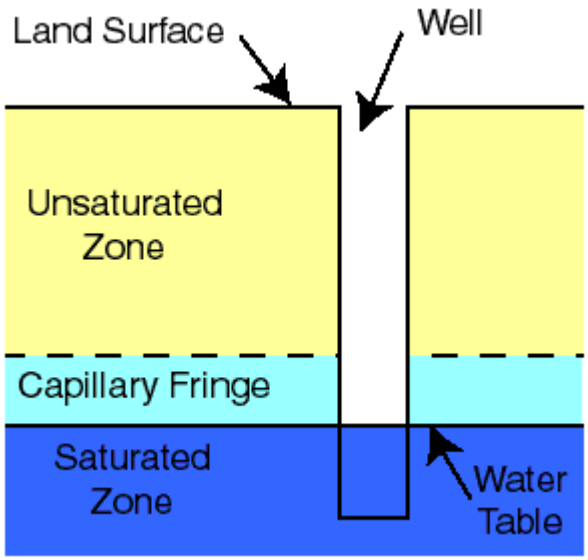

Figure 2.8 Subsurface environment showing the unsaturated and saturated zones (From USGS, 2006).

The unsaturated zone, also called the vadose zone, is the zone between the land surface and the regional water table (USGS, 2006). The pores in the unsaturated zone contain both water and air. The main distinguishing

feature of the unsaturated zone is that the pore water pressures are generally negative, i.e. less than the atmospheric pressure (Fetter, 1999; Sumner, 2000). As noted by the U.S Geological Survey, the unsaturated zone is a major focus of many contaminated site investigations because contaminants often have to pass through it to get to the groundwater or surface. Also, many contaminants are either accidentally placed or intentionally disposed of in the unsaturated zone (USGS, 2006).

The saturated zone is the zone below the water table. The pores in this zone are entirely filled with water hence the water content is equal to the total porosity (see Section 2.2.3.5). Here the water pressure is equal to or greater than the atmospheric pressure. Flow in this zone is predominately horizontal, with lesser components of flow in the vertical direction (Sumner, 2000). While gasoline may float on the water table due to their properties as discussed in Section 2.2.4, alcohol-blended gasoline may partly partition to groundwater due to cosolvent effect.

When released to the subsurface environment, contaminants are subjected to multiple processes, including phase distribution, sorption, transport, and biodegradation. Consequently, the following discussion on the fate of contaminants in the subsurface environment describes these processes, except biodegradation which was not examined in this study.

2.4.1 Phase distribution of contaminants

Once introduced into the vadose zone, organic contaminants in a nonaqueous phase liquid (NAPL) gradually partition into different phases based on their physicochemical properties (Yu, 1995). These phases include soil solids, soil water and soil air as shown in Figure 2.9. The

distribution of contaminants between these phases can be represented by empirical relationships referred to as partition coefficients (Huling and Weaver, 1991). Since the partition coefficients are highly site-specific and highly dependent on the characteristics of the soil (Section 2.2.3) and the contaminant (Section 2.2.4), the contaminant distribution between the phases can change with time and/or location at the same site. A good knowledge of the phase distribution of a contaminant released into the vadose zone could provide a significant insight in determining which tools are viable options with respect to site characterisation and remediation during alcohol-blended gasoline spills.

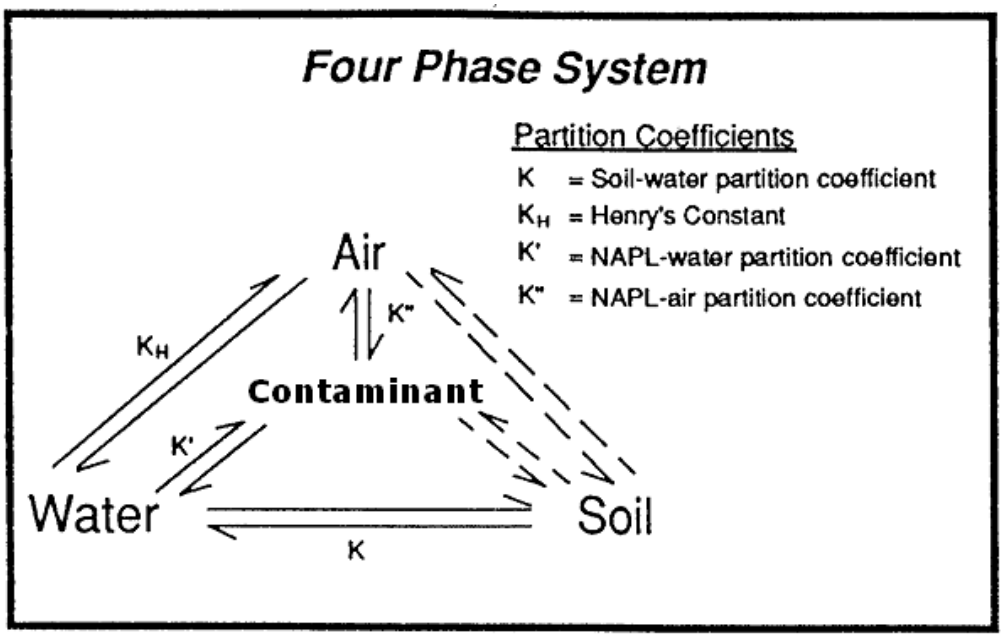

Figure 2.9 Distribution of contaminants in four phases in the vadose zone (Modified from Yu, 1995).

Nonaqueous phase liquid (NAPL) is usually the primary phase of contaminant being introduced to the subsurface in cases of spills and leaks. NAPL is further divided into "light" (LNAPL) and "dense" (DNAPL) based on the specific gravity of the NAPL relative to water (see Section 2.2.4.1). The

LNAPL have a specific gravity less than water, while the DNAPL have a specific gravity greater than water. Generally, gasoline compounds are classified as LNAPL. NAPL, both light and dense, migrates under the influence of gravity and capillary forces. Given time, it may penetrate the vadose zone and reach the groundwater, where it serves as a continuous source of contamination (Yu, 1995).

The soil solid phase or sorbed phase contaminants are in effect retained by the soil particles (Yu, 1995). It is commonly believed that the majority of sorbed contaminants are partitioned into organic matter on the soil particles surfaces, while a minor portion is adsorbed to inorganic or mineral surface features on the soil particles (see Section 2.2.3.7). In all, sorbed phase contaminant may comprise a significant part of the total contaminant mass, depending on the SOM content of the soil and the physicochemical property of the contaminant (Yu, 1995).

Soil water phase or dissolved phase contaminants occur due to the dissolution of the NAPL of contaminants in the vadose zone. The mass of a contaminant that exists in the soil water phase depends on the solubility of that contaminant (see Section 2.2.4.3). According to Newell et al. (1995), infiltrating precipitation and passing groundwater in contact with residual or mobile NAPL will dissolve soluble components and form an aqueous phase contaminant plume as shown in Figure 2.10. For a pure gasoline this effect might not be significant due to the hydrophobic nature of the gasoline compounds as highlighted in Sections 2.2.4.3 and 2.2.4.8. However, the effect may be significant for alcohol-blended gasoline due to the likely increase in the solubility of gasoline compounds with alcohol as discussed in Section 2.2.4.3. Although dissolved contaminants migrate with

the soil water, they usually do not move as fast as the soil water due to interactions with other phases (Yu, 1995).

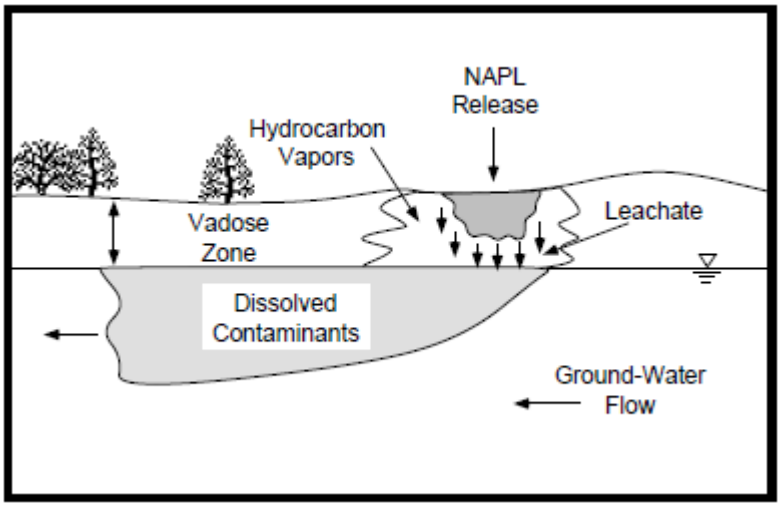

Figure 2.10 Dissolved and vapour phases of a released NAPL (Adapted from Newell et al., 1995).

The relative concentration of a contaminant in the soil air or vapour phase depends on its physicochemical properties, including density, solubility, vapour pressure and volatility (see Section 2.2.4). Contaminants with low density and high vapour pressure are likely to have a significant fraction in the vapour phase. The vapour phase is a highly mobile phase and migrates mainly via diffusion. It migrates much faster than the NAPL or the dissolved phase (Figure 2.10) (Dakhel et al., 2003; Pasteris et al., 2002; Yu, 1995). It can also migrate when the NAPL or dissolved phase migration has stopped (Yu, 1995). For example, the vapour phase from NAPL in the vadose zone has been reported as being responsible for the contamination of groundwater (Christophersen et al., 2005; Huling and Weaver, 1991). Addition of alcohol to gasoline can affect the fraction in the vapour phase. While ethanol may increase the fraction in the vapour phase due to its high

vapour pressure as discussed in Section 2.2.4.4, butanol may cause a decrease in the vapour phase fraction.

Although contaminants released to the vadose zone could be transported in vapour and liquid phases, this study focused on the vapour phase transport and fate of alcohol-blended gasoline compounds in the vadose zone. The use of the vapour phase is an established and effective method of investigating the fate and transport of volatile hydrocarbons in the vadose zone and has been adopted for fuel compounds studies by numerous researchers (Dakhel et al., 2003; Grathwohl et al., 2001; Höhener et al., 2006; Höhener et al., 2003; Karapanagioti et al., 2004; Lawrence et al., 2009; Mariano et al., 2009; McDowell and Powers, 2003; Österreicher-Cunha et al., 2009; Pasteris et al., 2002; Wang et al., 2003). More so, due to the high vapour pressure of gasoline compounds, a considerable portion of these compounds may exist as vapour in the subsurface environment. Finally, as already mentioned in the preceding paragraph, the vapour phase can spread much more efficiently than the NAPL or dissolved phase, and can also migrate toward groundwater when NAPL or dissolved-phase migration has stopped, hence, can be responsible for significant spreading of volatile contaminants in the vadose zone (Yu, 1995).

The mass of contaminants that partitioned to the soil air and soil water phases can be estimated from the vapour phase concentration by Equations [2.8] and [2.9] (Kerfoot, 1991).

$$M_a = C_a * V_a \qquad [2.8]$$

$$M_w = \frac{C_a}{H} * V_w \qquad [2.9]$$

where M_a and M_w are the masses of contaminant in the soil air and water phase, respectively, C_a is the concentration of contaminant in the soil air, V_a and V_w are the volumes of air and water in the soil system, respectively, and H is the dimensionless Henry's law constant.

For a closed soil system where the total mass (M_t) of contaminant released to the soil and the mass extracted for analysis (M_L) are known, the mass adsorbed on the soil solids (M_s) can be estimated by a simple mass balance using Equation [2.10].

$$M_s = M_t - (M_a + M_w) - M_L \qquad [2.10]$$

Integrating Equations [2.8] and [2.9] into Equation [2.10] yields Equation [2.11].

$$M_s = M_t - C_a\left(V_a + \frac{V_w}{H}\right) - M_L \qquad [2.11]$$

Thus, by knowing the soil air concentration of contaminants in a closed soil system, the mass distribution to the air, water and solid phases can reasonably be estimated. As can be seen in Equation [2.11], the higher the value of H for a contaminant the lower the amount that partitions to the soil water, hence, the higher the amount that adsorbs to the soil solids. Therefore, in agreement with existing literature as discussed in Section 2.2.4.5, the value of H in Equation [2.11] gives an indication of the hydrophobicity of contaminants.

2.4.2 Sorption of contaminants

Sorption is a mass-transfer process that results in the migration of contaminants from a liquid phase to an adjacent solid phase, an interface or a second fluid phase (Adamson, 1990). The term sorption comprises absorption and adsorption processes. Absorption is the inter-phase dissolution of solute molecules resulting from their complete mixing throughout the sorbent phase. Adsorption, on the other hand, is a surface phenomenon and refers to mass-transfer of a solute from a fluid to the surface of a solid or its accumulation at the interface between two phases. Adsorption processes can be further classified as physisorption where solute-sorbent interactions are primarily due to weak van der Waals forces, and chemisorptions where stronger chemical bond formations occur between the solute and sorbent surfaces. Sorption processes affect the fate of the contaminants in the subsurface environment by complex combination of absorption, physisorption and chemisorption reactions with soil components controlling mobility, bioavailability, toxicity and fate of organic contaminants in soils (Bhandari et al., 2007).

Previous studies have shown that the sorption of contaminants on soil is related to the SOM content of the soil and that the contribution of soil minerals is minor (Celis et al., 2006; Chen et al., 2007; Chiou, 2002; Huang and Weber, 1997; Shi et al., 2010). Among the soil minerals, hydroxyl surfaces, as found on gibbsites, sorb more efficiently than oxygen surfaces, as found on montmorillonite (Site, 2001). The association of contaminants to SOM has been attributed to hydrophobic bonding. This type of bonding is due to the combination of van der Waals forces and a thermodynamic gradient driving contaminants of low solubility out of solution, because the interactions of these contaminants with SOM are energetically preferred to compound-water or compound-compound

interactions (Weber Jr et al., 1991). However, not only the concentration of SOM plays an important role in the sorption of organic compounds, the SOM composition does as well. It has been reported that both the concentration and composition of SOM significantly affected the sorption of atrazine (Site, 2001). Also, the sorption-desorption behaviour of atrazine in two different soils have been found to be affected by the amount and location of the associated SOM (Lesan and Bhandari, 2003).

Furthermore, it has been found that the presence of other liquids in a soil may significantly change the sorption phenomenon of contaminants. For instance, the sorption of neutral organic compounds, such as naphthalene, phenanthrene and diuron, was found to decrease in the presence of an organic cosolvent, such as methanol (Bouchard, 1998). Also, the amount of toluene sorbed from a hydrocarbon mixture was found to be smaller than the amount of toluene sorbed from a single hydrocarbon solution, showing thereby a competitive sorption in a mixture of hydrocarbons (Site, 2001). Pignatello et al. (2006) in their nonlinear and competitive sorption study noted that sorption would be competitive when two solutes are present together. Such competitive sorption could be due to either differences in sorption energies due to sorbent or solute heterogeneity, or sorption site limitations (Weber Jr et al., 1991). The magnitude of the sorption depends upon the quality and quantity of the sorbent, as well as the co-solute concentrations (Allen-King et al., 2002). Thus, the addition of either ethanol or butanol to gasoline may change the sorption of the gasoline compounds. Knowing the extent of this change would be important in predicting the fate and transport for alcohol-blended fuels.

2.4.2.1 Sorption coefficient (K_d)

Sorption coefficient (K_d) relates to the distribution of contaminants between the soil water and soil solids (Site, 2001). The K_d value for a contaminant depends on the nature of the solid and the physicochemical properties of the contaminant (Site, 2001; Weber Jr et al., 1991). The K_d values of a range of contaminants have been found to depend linearly on the SOM content in soil (Celis et al., 2006; Chen et al., 2007; Chiou, 2002; Shi et al., 2010). Generally, the K_d value of a contaminant is estimated by Equation [2.12] (Kerfoot, 1991; Vallero, 2004).

$$K_d = \frac{C_s}{C_w} \qquad [2.12]$$

where C_s is the concentration of gasoline compound in soil (µg/kg) and C_w is the concentration of gasoline compound in water (µg/L).

C_s and C_w are estimated as shown in Equations [2.13] and [2.14], respectively (Kerfoot, 1991).

$$C_s = \frac{M_s}{M_{ts}} \qquad [2.13]$$

$$C_w = \frac{C_a}{H} \qquad [2.14]$$

where M_{ts} is the total soil mass.

Incorporating Equations [2.11], [2.13] and [2.14] into Equation [2.12] yields Equation [2.15].

$$K_d = \frac{H}{C_a M_{ts}}\left(M_t - C_a V_a - \frac{C_a V_w}{H} - M_L\right) \quad [2.15]$$

From Equation [2.15], the sorption coefficient of a contaminant can be estimated from its vapour concentration. More so, the K_d of a contaminant can reasonably be estimated for soils at 0% water content, i.e. when V_w = 0.

Coupled with other contaminant properties such as Henry's law constant, sorption coefficient has been noted as a vital parameter in modelling the overall distribution of organic contaminants in the environment (Boethling and Mackay, 2000). Although there are variety of models, such as Linear, Langmuir and Freundlich, commonly used to describe the phase distribution of organic contaminants between water and solid phases (Weber Jr et al., 1991), the linear and Langmuir models have been shown to be useful when the vapour phase of contaminants is investigated, as done in this work (Kerfoot, 1991; Ong and Lion, 1991). However, the Langmuir model is commonly used for mineral dominated sorption rather than the organic dominated sorption examined in this work (Boethling and Mackay, 2000). In addition, at low contaminant concentration, as used in this work, the linear model has been found to be adequate in describing sorption by soils (Boethling and Mackay, 2000; Weber Jr et al., 1991).

2.4.2.2 Retardation factor (R)

Retardation factor (R) relates to the extent that the migration of a contaminant in the subsurface environment is retarded as a result of sorption and is expressed in Equation [2.16] (Hemond and Fechner-Levy,

2000; Logan, 2012; Mehran et al., 1987; Myrand et al., 1992; Rivett et al., 2001; Site, 2001):

$$R = 1 + \left(\frac{\rho}{n}\right) K_d \qquad [2.16]$$

where ρ is the bulk density of the vadose zone material (g/mL), n is the porosity of the vadose zone (dimensionless) and K_d is the sorption coefficient of contaminant (mL/g).

It has been reported that the migration of contaminants in the subsurface environment increased with decreasing R values (Rivett et al., 2001). Also, it has been found that the hydrophobicity of organic compounds correlated with their R values, with highly hydrophobic compounds having high R values and less hydrophobic compounds having low R values (Rivett et al., 2001). Hence, R is a key parameter in the study of the environmental fate of organic compounds that indicates the transfer rate of organic compounds in the subsurface environment.

2.4.3 Transport of contaminants

2.4.3.1 Infiltration

Infiltration is a key process that determines the quantity of a contaminant spill that enters the soil while the rate at which infiltration occurs will depend on the state of dryness or wetness of the soil, pore size distribution and hydraulic conductivity of the soil (Sumner, 2000). As illustrated by Powers et al. (2001b), the infiltration of gasoline through the vadose zone is one of the transport processes that affects its transport in the subsurface as shown in Figure 2.11. When released to the soil, either from leaks or

spills, gasoline infiltrates down through the unsaturated zone due to gravity. This is accompanied to some extent by lateral spreading due to the effect of capillary forces and medium spatial variability, with a fraction of it being retained in the pore spaces due to interfacial forces. This creates a residual saturation of gasoline that generally occupies 1 - 7% of the pore space in the unsaturated zone (Meyers, 1999; Powers and McDowell, 2001; UTTU, 2003). The transport of the gasoline in the subsurface is affected by the following factors: (1) volume of gasoline released, (2) properties of the gasoline, (3) properties of the media, (4) subsurface flow conditions, (5) time duration of release, and (6) area of infiltration (Meyers, 1999). The presence of oxygenate, such as ethanol, can potentially change two properties that control the fate of gasoline in the subsurface (Powers et al., 2001b; Powers and McDowell, 2001; UTTU, 2003). Firstly, the partitioning of petroleum hydrocarbons is increased, leading to an increased flux of contaminants to the groundwater. Secondly, the surface and interfacial tensions that cause interfacial forces, which result in entrapment of residual gasoline in the unsaturated zone, are reduced, leading to less capillary entrapment. The researchers noted that the changes occur due to the differences in the hydrophobicity of ethanol relative to gasoline components. However, as noted by Nzengung et al. (1997), such cosolvent effects on contaminants (Section 2.2.4.3) would depend on contaminants structure, the cosolvent (oxygenate) fraction, and the nature of soil that may alter the diffusion.

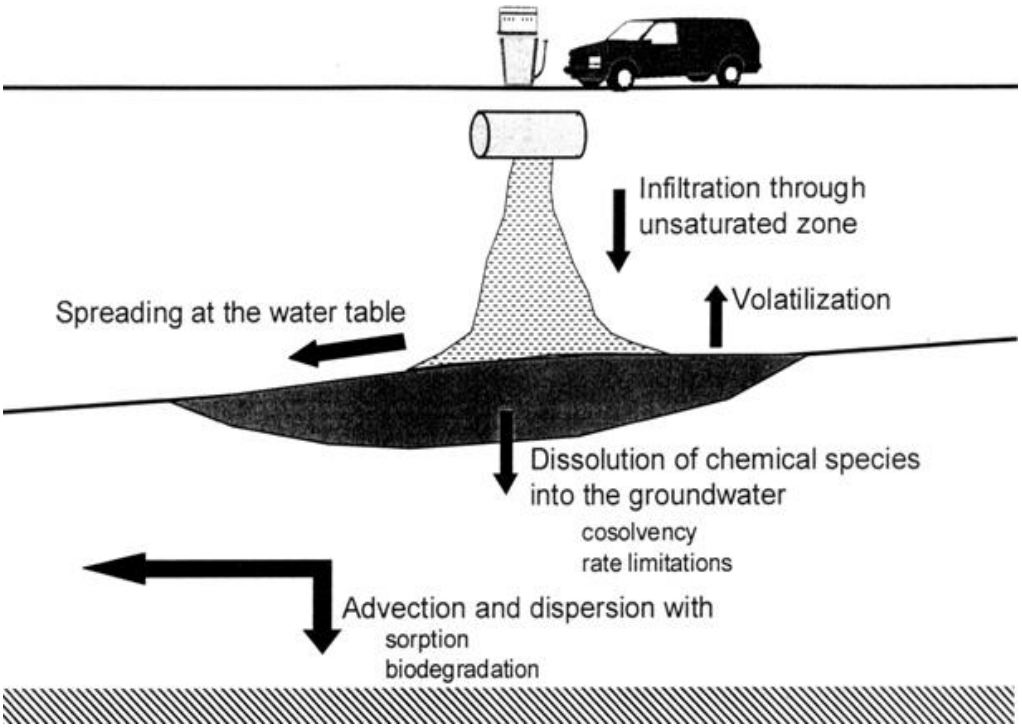

Figure 2.11 Transport processes governing the transport of gasoline in the subsurface environment (Adapted from Powers et al., 2001b).

2.4.3.2 Diffusion

Studies have shown that contaminants, such as hydrocarbons, can be transported from the unsaturated zone to the groundwater via diffusion (Dakhel et al., 2003; Hemond and Fechner-Levy, 2000; Lahvis, 2003; Pasteris et al., 2002; Powers and Heermann, 1999). According to Yu (1995), diffusion is a major driving force behind subsurface contaminant transport. Diffusion is readily observed in the subsurface environment and the larger the amount of contaminant the larger and farther the effects of diffusion can be (Miller and Hogan, 1997). Other factors affecting diffusion rate are the properties of the contaminants (Section 2.2.4) and the soil (Section 2.2.3). In the soil, the diffusion of contaminants is impacted by the tortuosity of diffusion paths (Bhandari et al., 2007). The vapour phase transport of contaminant in the vadose zone is dominated by diffusion (Yu,

1995). Hence, diffusion can be detected by observing the changes in vapour phase.

2.5 Soil and groundwater contamination monitoring techniques

Accurate estimation of the scale and fate of contamination in any environmental media, mainly soil and groundwater, requires that samples be obtained from the media using appropriate sampling and contamination monitoring techniques that produce representative samples for analysis. In the past years, a number of techniques have been employed by researchers for monitoring soil and groundwater contaminants movement. These can be broadly grouped into laboratory and field techniques.

2.5.1 Laboratory techniques

Laboratory techniques are the techniques used in the laboratory for monitoring soil and groundwater contaminant movement. So far, three main techniques have been used in the laboratory to monitor soil and groundwater contamination. These include column, microcosm and tank experiments.

2.5.1.1 Column experiment

Column experiments entail the use of a column, such as a cylindrical tube, positioned horizontally with both ends sealed (Höhener et al., 2003). The contaminant is injected into one end of the tube and monitored as it migrates within the tube to the other end, using the sampling ports located at various positions along the tube as shown in Figure 2.12. Studies on

gasoline or gasoline blends that used column as the experimental system include studies by Li and Voudrias (1994), Höhener et al. (2003), McDowell and Powers (2003), Wang et al. (2003) and Höhener et al. (2006). The various synthetic gasoline mixtures used in these studies are compared in Table 2.6. These studies have shown that column experiments can reasonably be used to investigate the transport, sorption and biodegradation of fuel compounds in soil. However, column studies investigate only the horizontal migration of contaminants, which is usually negligible in the unsaturated zone of natural environment. As discussed in Section 2.4.3.1, contaminants are transported downward towards the saturated zone following release. Besides, since this work looks at groundwater contamination risks for alcohol-blended gasoline vapours, it requires an experimental system that simulates both the unsaturated zone and the underlying groundwater zone. Therefore, the column system may not be suitable for this study and data obtained from it might not be applicable to the field.

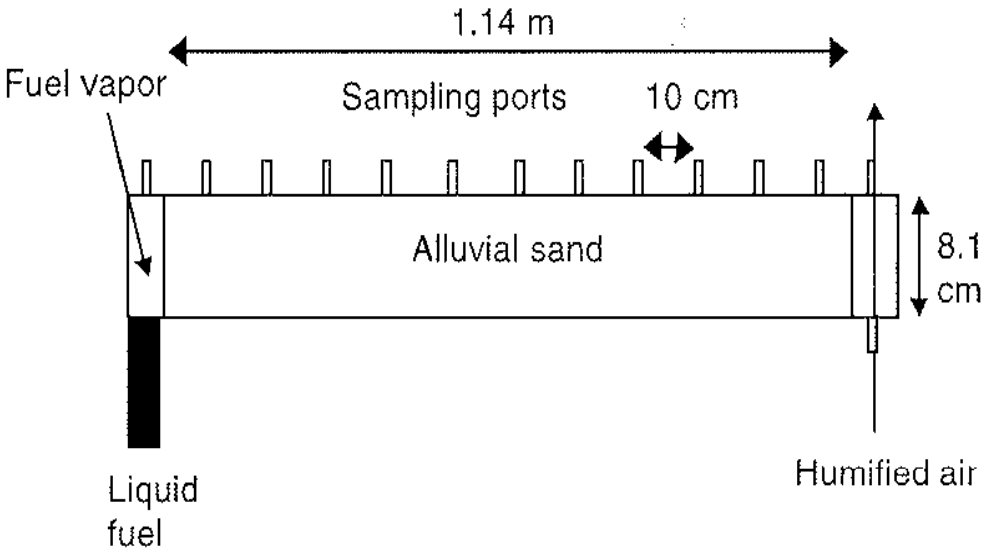

Figure 2.12 Column experimental setups for liquid fuel vapour transport experiments (Adapted from Höhener et al., 2003).

Table 2.6 Fuel compound mixture used by various researchers.

Researcher	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fuel compound mixture used	Toluene EB MCH MTBE TCE	Pentane Hexane Octane Decane Dodecane MCP MCH CH Isooctane Toluene m-Xylene 1,2,4-TMB MTBE	Pentane Hexane Octane Decane Dodecane MCP MCH CH Isooctane Benzene Toluene m-Xylene 1,2,4-TMB MTBE Ethanol	Pentane Hexane Octane Decane Dodecane MCP MCH CH Isooctane Toluene m-Xylene 1,2,4-TMB MTBE	Isooctane ethanol	**Mixture 1** MTBE MCH Toluene EB **Mixture 2** MCH Toluene EB 1,1,1-TCA TCE PCE	Benzene Toluene m-Xylene 1,2,4-TMB Hexane Octane Decane Dodecane MCP CP MCH Isooctane 3-MP	Hexane Octane Decane Dodecane CP MCP MCH 3-MP Isooctane Benzene Toluene m-Xylene 1,2,4-TMB	**Mixture 1** Benzene Toluene o-Xylene **Mixture 2** Benzene Toluene o-Xylene Ethanol	**Mixture 1** Benzene Toluene EB Xylenes Heptane **Mixture 2** Benzene Toluene EB Xylenes Heptane Ethanol

Researcher: 1. Grathwohl et al. (2001); 2. Pasteris et al. (2002) & Karapanagioti et al. (2004); 3. Dakhel et al. (2003); 4. Höhener et al. (2003); 5. Mcdowell and Powers (2003); 6. Wang et al. (2003); 7. Christophersen et al. (2005); 8. Höhener et al. (2006); 9. Mackay et al. (2006); 10. Österreicher-Cunha et al. (2009).

Fuel compound: EB - Ethylbenzene; MCH - Methylcyclohexane; MTBE - Methyl-tert-butyl ether; TCE - Trichloroethene; MCP - Methylcyclopentane; CH - Cyclohexane; Isooctane - 2,2,4-trimethylpentane; 1,2,4-TMB - 1,2,4-Trimethylbenzene; 1,1,1-TCA - 1,1,1-Trichloroethene; PCE - Tetrachloroethene; CP - Cyclopentane; 3-MP - 3-Methylpentane.

2.5.1.2 Microcosm experiment

A microcosm is a glass vial with a mininert valve comprising sampling port and rubber septum as shown in Figure 2.13 (Miles and Doucette, 2001). The mininert valve serves as both injection and sampling port. Studies that used microcosm, especially those on gasoline and gasoline blends, were carried out by Höhener et al. (2006; 2003), Lawrence et al. (2009), Mariano et al. (2009) and Österreicher-Cunha et al. (2009). These studies have demonstrated that microcosm can be used to investigate the distribution, sorption and biodegradation of gasoline compounds in the unsaturated zone, as well as contaminant motivated microbial community shifts in the soil. Other studies that used microcosm as the experimental system include studies by Werner and Höhener (2003), Chen et al. (2007), Joo et al. (2008) and Shi et al (2010). These studies evaluated the contributions of the various soil components to the overall sorption of a range of hydrophobic organic compounds, including individual gasoline compounds, but not in a combination that simulates gasoline or gasoline blends. Microcosm experiments are usually simple, inexpensive, reproducible, consistent and applicable to a wide variety of volatile and semivolatile organic compounds (Miles and Doucette, 2001). Although microcosm experimental data cannot be applied directly to field situations, the data provide reasonable indication of what may happen in the field (Österreicher-Cunha et al., 2009).

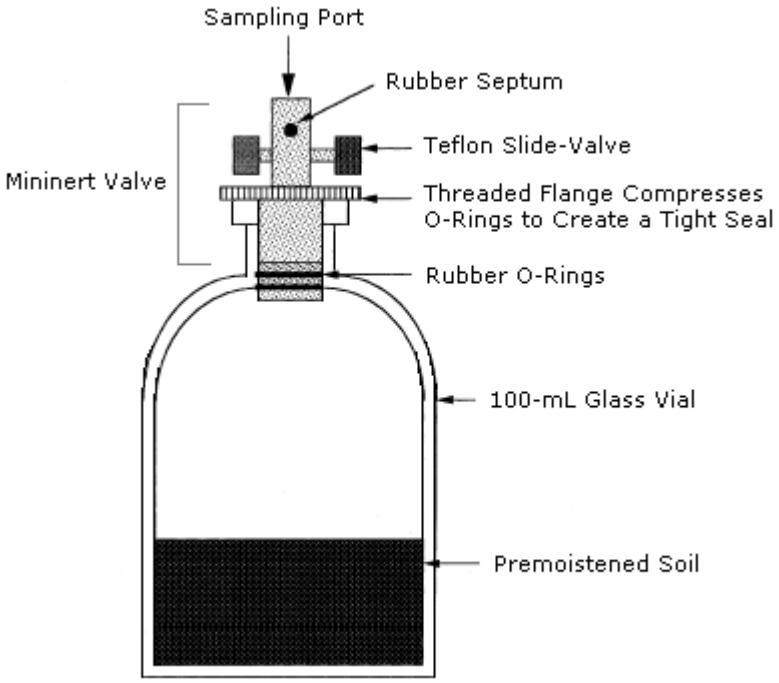

Figure 2.13 A microcosm experimental setup (From Miles and Doucette, 2001).

2.5.1.3 Tank experiment

A tank experiment involves the use of a tank, usually a transparent glass container, without injection and sampling ports as shown in Figure 2.14 (McDowell and Powers, 2003). The contaminant is either injected at the top of the tank or injected at a defined depth within the tank. This allows visual monitoring of its migration and behaviour. Studies by Grathwohl et al. (2001) and McDowell and Powers (2003) are examples of studies on gasoline and gasoline blends conducted using tank as the experimental system. While Grathwohl et al. (2001) used the tank system to study the natural attenuation of volatile hydrocarbons in the unsaturated zone, McDowell and Powers (2003) used it to examine the differences in the behaviour of a gasoline and a 10% ethanol-blended gasoline (E10) as they infiltrate through the simulated vadose zone. However, with the use of a tank system, only general information on the migration and behaviour of

the contaminants can be obtained. Information on the migration and behaviour of the individual constituents of the contaminant cannot be obtained.

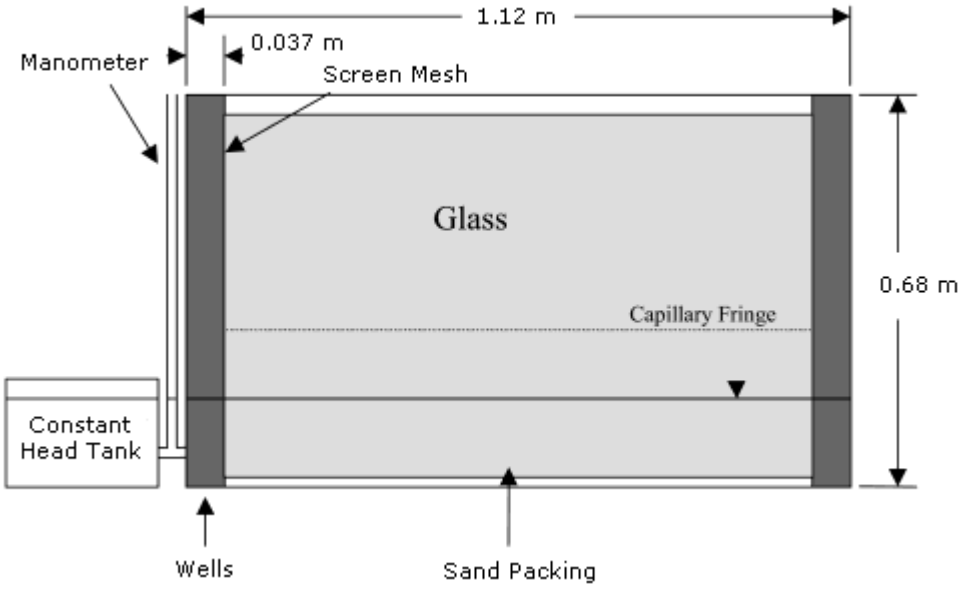

Figure 2.14 Schematic diagram of a tank experimental setup (From McDowell and Powers, 2003).

2.5.2 Field techniques

Field techniques are the techniques used in the field for monitoring soil and groundwater contamination. Thus far, two techniques have been successfully used. These include lysimeter and emplacement experiments.

2.5.2.1 Lysimeter experiment

Figure 2.15 shows the schematic of a typical lysimeter experimental setup. Several studies on fate and transport of contaminants, particularly gasoline and gasoline blends, in the field have been conducted using lysimeter (Dakhel et al., 2003; Karapanagioti et al., 2004; Pasteris et al., 2002).

Both Pasteris et al. (2002) and Karapanagioti et al. (2004) used the lysimeter to examine the vapour phase transport and biodegradation of gasoline compounds in the unsaturated zone, while Dakhel et al. (2003) used the system to investigate the fate of spilled gasoline containing both ethanol and MTBE in the unsaturated zone. Although lysimeter produces data which are applicable to the field, its gigantic size as well as the associated complexity makes it difficult to manage, and thus makes data generated from it difficult to reproduce. However, by scaling down the lysimeter to a manageable size that reduces complexity, it can be used in the laboratory to generate data which will be applicable to the field as done in this study.

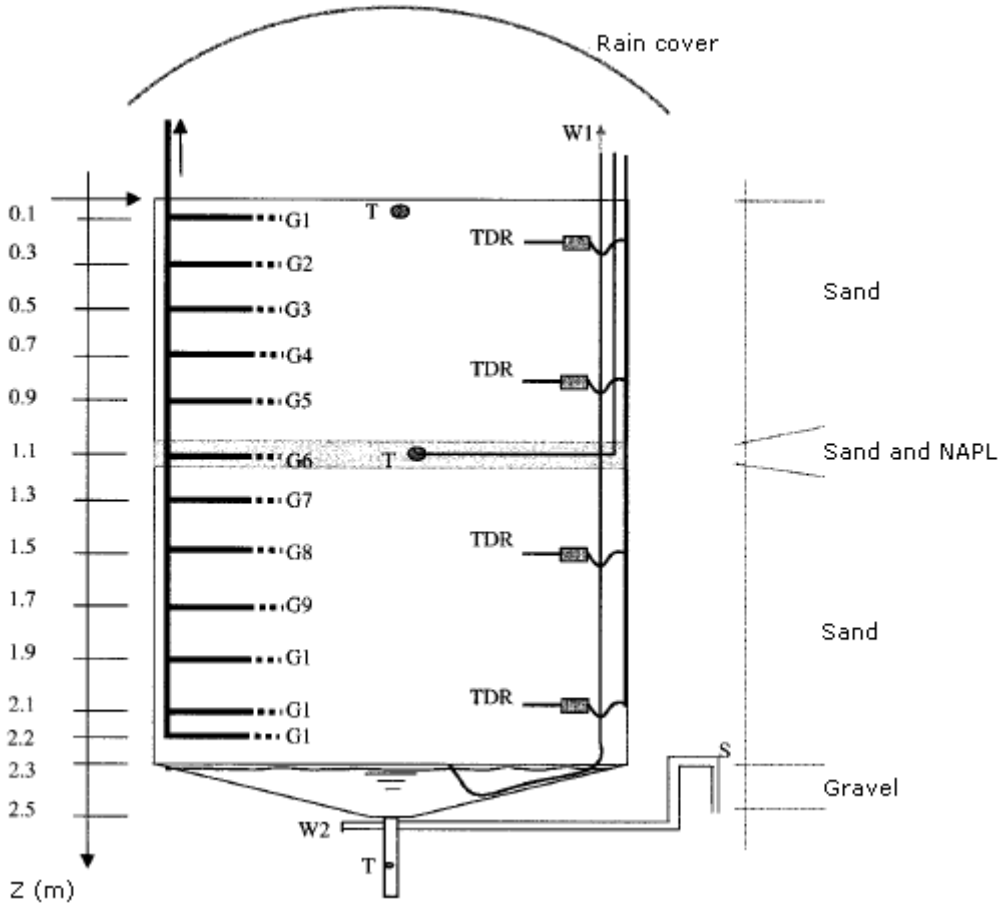

Figure 2.15 Schematic drawing of a lysimeter experimental setup (From Pasteris et al., 2002).

2.5.2.2 Emplacement experiment

Emplacement experiments involve the contaminants of interest being injected or placed at a defined depth below ground surface at a chosen site where the migration and degradation of the contaminants are monitored through monitoring wells or gas probes located at defined distances and directions with respect to the source zone (Werner et al., 2005; Zhang et al., 2006). A typical emplacement experiment is described schematically in Figure 2.16 where studies on fate and transport of gasoline and gasoline blends have been conducted (Christophersen et al., 2005; Höhener et al., 2006; Mackay et al., 2006). Although the emplacement technique simulates the natural environment perfectly, cost and weather conditions could be a hindrance to its successful application. Besides, it cannot be replicated in the laboratory.

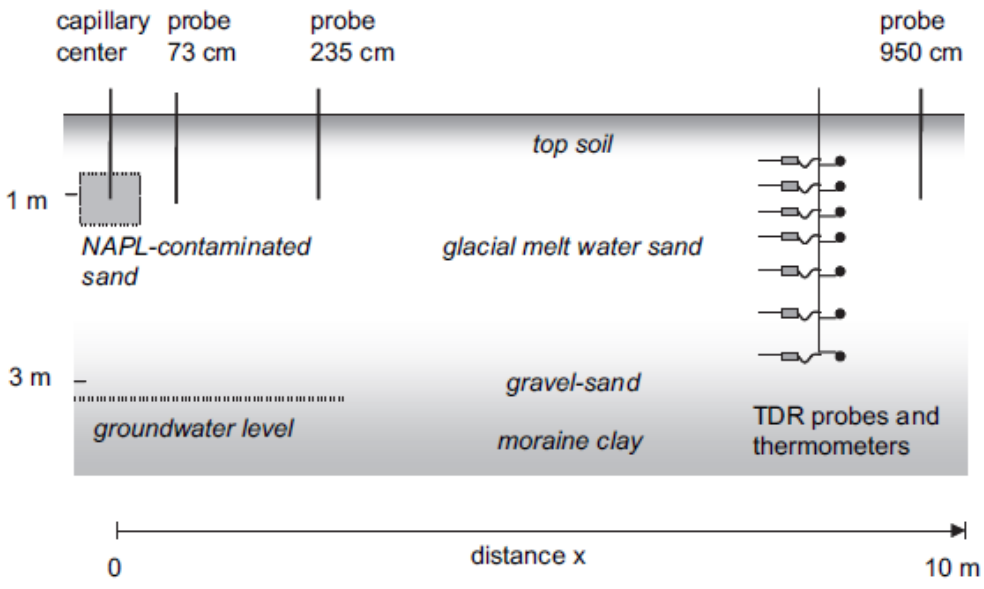

Figure 2.16 Schematic diagram of an emplacement experiment (From Werner et al., 2005).

2.5.3 Summary of setups

Laboratory techniques, such as column, microcosm and tank experiments, and field techniques, such as lysimeter and emplacement experiments, have been used to study the fate and transport of gasoline and gasoline blends in the subsurface environment. Among the laboratory techniques, the microcosm has been extensively used due to its benefits, such as being simple, inexpensive, reproducible, consistent, applicable to a wide variety of organic compounds, and provides reasonable indication of what may happen in the field. Hence, microcosm has been used in this study to obtain data on sorption and phase distribution of gasoline compounds in the vadose zone.

However, microcosms cannot provide direct information on the vapour phase transport of contaminants in the vadose zone, but the field techniques can. Among the field techniques, lysimeter has been widely used and simulates the natural environment very well. However, it cannot be used directly in the laboratory due to its large size. Therefore, this study has scaled down a lysimeter to a dimension that can be accommodated in the laboratory, which will be one way of harmonizing the benefits of laboratory and field techniques and thus generating data in the laboratory which will be applicable to the field. Thus, the microcosm and a scaled down lysimeter, called mini-lysimeter, have been designed, commissioned and used in this study.

2.6 Contaminants detection and quantification equipment

Presently, the most commonly used equipment for the detection and quantification of organic compounds include gas chromatography (GC), mass spectrometer (MS) and gas chromatography/mass spectrometer. In this study, an MS directly attached to the mini-lysimeter and a GC for the microcosm experiments were used for real-time measurements.

2.6.1 Gas chromatography

Gas chromatography (GC) separates different volatile compounds using a column where this separation allows detection and quantification of the individual compounds in the sample based on their volatility and structure (Rood, 2007). For a compound to be suitable for GC analysis, it must possess significant volatility at temperatures below 350 – 400 ^{o}C and swiftly transformed into a vapour without degradation or reacting with other compounds (Rood, 2007). Consequently, most organic compounds, including hydrocarbons, are suitable for GC analysis. A GC system consists of six major components, namely gas supply and flow controllers, injector, detector, oven, column, and a data system as shown in Figures 2.17. Generally, the suitability of a GC towards analysing a sample depends on the column and the detector (Rood, 2007). The column consists typically of a stationary phase that obstructs the movement of each compound down the column by a different amount thereby controlling retention time. The length and diameter of the column, the chemical structure and amount of the stationary phase, and the column temperature all affect the compound retention. Although each detector differs in design and performance, however, the principle of operation is the same and a general set of rules

and characteristics apply to all. The detector interacts with compounds based on some physical or chemical properties. This interaction generates an electrical signal whose size corresponds to the amount of the compound. Among the available detectors, the most commonly used, especially for the separation of samples containing hydrocarbons, is Flame Ionization Detector (FID). As noted by McMaster (2008), GC suffers from a few weaknesses. The major weakness is the lack of definitive proof of the nature of the detected compounds. This is true as identification is based solely on retention time which could be the same for many compounds. Another weakness is its requirement for only volatile compounds.

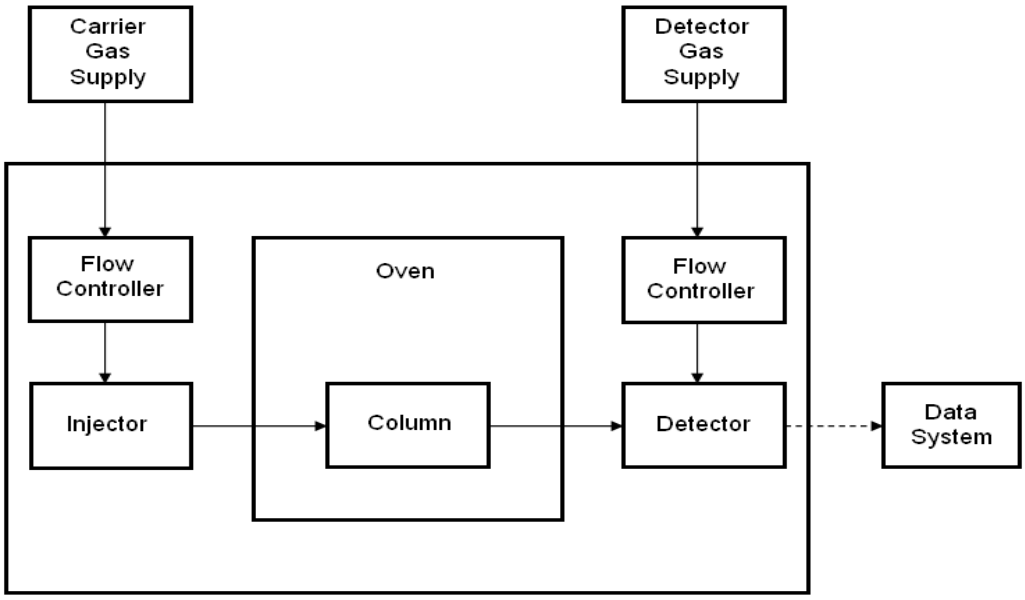

Figure 2.17 Block diagram of a typical gas chromatography (From Rood, 2007).

2.6.2 Mass spectrometer

A mass spectrometer (MS) is an instrument for generating gas-phase ions, separating them according to their mass-to-charge ratio (m/z) using electric fields, or sometimes magnetic fields, in an evacuated volume

where the number of ions is detected (Henderson and McIndoe, 2005). A typical MS system consists of an ion source, mass analyser, detector and a data acquisition system as shown in Figure 2.18. The sample to be analysed is injected into the ion source where it is ionized. The ions are then transported to the mass analyser where they are separated according to their m/z ratios. The separated ions are detected, registered and counted by the detector and the resulting signal is sent to a data system for processing. A display of the signal generated by the sorted ions is presented as the mass spectrum.

Although MS has a definitive proof of the nature of the detected compounds (Davis and Frearson, 1987), it also suffers from a few weaknesses. The major weakness is the inability to analyse accurately samples containing compounds having close molecular masses. There is usually the problem of overlaps, which leads to errors in data processing when analysing compounds with similar molecular masses. However, sophisticated programs can now analyse the MS trace and quantify these compounds. Also, MS requires high vacuum for operation. According to Henderson and McIndoe (2005), the high vacuum minimises ion-molecule reactions as well as scattering and neutralisation of the ions. In addition, the MS must be tuned and calibrated before meaningful data can be obtained (McMaster, 2008). Provided these factors are met, MS can give real-time analysis of the gas phase during sampling.

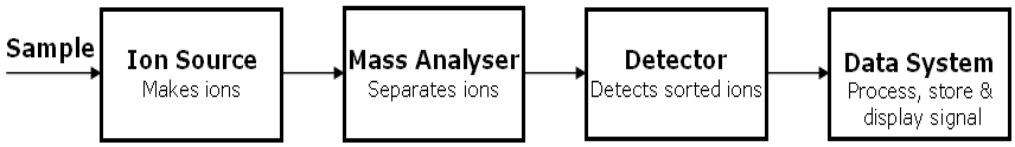

Figure 2.18 Block diagram of a typical mass spectrometer system (Modified from Davis and Frearson, 1987).

2.7 Research justification

The review of available literature has shown that laboratory and field techniques have been used to study the fate and transport of gasoline compounds in the vadose zone. Laboratory techniques do not simulate the natural environment well enough, hence data obtained from them are assumed as indications of what may happen in the field. Conversely, a lysimeter field technique simulated the natural environment well but cannot be used in the laboratory due to its bulky size. Therefore, scaling down the lysimeter to a dimension that can be accommodated in the laboratory as proposed in this research will be one way of harmonizing the benefits of laboratory and field techniques and thus generating data in the laboratory which will be applicable to the field.

While significant advances have been made towards understanding the fate and transport of ethanol-blended gasoline in the vadose zone, little attention has been given to how SOM will impact the fate and transport of ethanol-blended gasoline in the vadose zone. Therefore, it is still unclear how SOM will impact the sorption and phase distribution of a complex mixture like ethanol-blended gasoline in the vadose zone after release. Studies on butanol-blended gasoline have focused on biodegradation with little attention on sorption and phase distribution in the vadose zone. Also, no information is available on how SOM will impact the fate and transport of butanol-blended gasoline in the vadose zone. A good knowledge of the impact of SOM on the fate and transport of alcohol-blended gasoline, as aimed to achieve in this research, will be crucial for the successful development of fate and transport models for alcohol-blended gasoline compounds in vadose zones with varying SOM contents.

When added to gasoline as oxygenate, butanol and ethanol have been compared for miscibility with gasoline, phase separation in the presence of water, and distribution through pipelines. However, it is still unknown which blend will cause higher groundwater contamination after spills. This knowledge will be invaluable in making informed decision on which of the alcohols to adopt as future gasoline oxygenate. Therefore, this research is aimed to fill these knowledge gaps.

CHAPTER THREE

3. EXPERIMENTAL

This chapter presents a detailed explanation of the materials, experimental systems and equipment used in this research.

3.1 Alcohol/gasoline blends composition

The alcohol/gasoline blends used in this study were synthetic gasoline blended with 0% to 20% ethanol or butanol, referred to as UG for unblended gasoline, E0 to E20 and B0 to B20, respectively. The ethanol (>99.5%) and butanol (99.8%) were purchased from Sigma-Aldrich chemical company, UK. The synthetic gasoline sample was prepared from six typical gasoline compounds as listed in Table 3.1 and based on the mixture used elsewhere in the literature as shown in Table 2.6 in Section 2.5. The six gasoline compounds were all of high purity (>99.5%) and were purchased from Sigma-Aldrich chemical company, UK. The selected gasoline compounds are typical constituents of petroleum fuel (Christophersen et al., 2005; Höhener et al., 2003; Pasteris et al., 2002; Speight, 2002) and represent the three major hydrocarbon groups in gasoline, namely alkanes (or paraffins), cycloalkanes (or naphthenes) and aromatics (Sections 2.3.1 and 2.3.2). The weight percentages of the gasoline compounds were chosen according to the typical fuel composition noted by Pasteris et al. (2002) and Höhener et al. (2003). The use of synthetic gasoline was necessary to eliminate the problem of unknown composition usually encountered with the use of commercial gasoline (Powers et al., 2001b). The high blending of 20% alcohol by volume was motivated by the consistent increase in the utilization of ethanol as

gasoline oxygenate around the world as illustrated in Figure 1.1 in Section 1.1.

The concentration of each gasoline compound in the gas phase for the alcohol/gasoline blends used was calculated based on the initial mole fraction and vapour pressure governed by Raoult's law as expressed in Equation [3.1] (Höhener et al., 2003; Pasteris et al., 2002).

$$C_g = \frac{P^o X}{RT} * MW \qquad [3.1]$$

where C_g is the concentration in gas phase (g/m^3), P^o is the vapour pressure (atm), X is the mole fraction, R is the universal gas constant ($8.21*10^{-5}$ $m^3 atm K^{-1} mol^{-1}$), T is the temperature (K), and MW is the molecular weight (g/mol).

The C_g of each gasoline compound was converted to the desired unit of g/mL by dividing result in g/m^3 by 10^6 since 1 m^3 is equal to 0.001 L and 1 L is equal to 0.001 mL. Table 3.2 summarises the calculated concentration of each gasoline compound in the gas phase for the alcohol/gasoline blends used.

Table 3.1 Synthetic gasoline composition.

Gasoline compound	**Formula**	**Weight in mixture, %**	**Volume, mL**	**Vapour pressure at 20°C, Pa**[a]	**Density at 25°C, g/mL**[a]	**Henry's law constant, -**[c]	**Water solubility at 25°C, g/L**[c]
Pentane	C_5H_{12}	9.6	15.3	57900	0.626	51.4	0.04
Octane	C_8H_{18}	25.8	36.7	1470	0.703	211	0.0004
MCP	C_6H_{12}	19.5	26.0	17732[b]	0.75	14.7	0.04
MCH	C_7H_{14}	32.3	41.9	4930	0.77	17.5	0.01
Benzene	C_6H_6	3.2	3.7	9950	0.874	2.26E-01	1.76
Toluene	C_7H_8	3.2	11.1	2910	0.865	2.65E-01	0.54
			Gasoline additive				
Ethanol	C_2H_5OH	-	0 - 20%	5950	0.789	2.94E-04	Total
Butanol	C_4H_9OH	-	0 - 20%	500	0.81	4.99E-04	80.61

MCP – Methylcyclopentane; MCH – Methylcyclohexane; [a] values obtained from Sigma Aldrich Material Safety Data Sheet; [b] value obtained from Pasteris et al. (2002) Supporting Information; [c] obtained from Yaws (2008)

Table 3.2 Calculated concentration of each gasoline compound in the gas phase for the alcohol/gasoline blends used.

Fuel compound	Concentration in gas phase (g/mL)				
	UG	E10	E20	B10	B20
Pentane	2.43E-04	1.96E-04	1.58E-04	2.10E-04	1.81E-04
MCP	1.29E-04	1.04E-04	8.39E-05	1.12E-04	9.62E-05
MCH	6.61E-05	5.34E-05	4.29E-05	5.74E-05	4.91E-05
Benzene	1.53E-05	1.24E-05	9.84E-06	1.33E-05	1.13E-05
Toluene	1.31E-05	1.06E-05	8.51E-06	1.14E-05	9.75E-06

Note: UG = E0 = B0

3.2 Soil composition

The soil used in this study comprised a mixture of sand and peat as the source of SOM. The sand was obtained from Nottingham (UK) and contained <0.1% SOM. The sand was oven dried and had a particle size distribution of coarse (20%), medium (53%) and fine (27%). According to the BS1377-1 (1990) soil classification in Section 2.2.3.2, the sand could be classified as a fine-grained sandy soil. The peat was also obtained from Nottingham (UK) and contained ≈96% SOM in its dry state, as determined by the "Loss on Ignition" (LOI) method as described later in Section 3.2.1. The peat was sieved through a 2 mm sieve to obtain particles generally regarded as SOM (Page, 1982).

The sand and the peat were mixed on a dry basis to obtain soil consisting of 0 - 5% SOM by weight. These percentages of SOM were chosen because they are within the reported range of SOM fraction for typical soils (Bohn et al., 2001; Sparks, 2003). The use of sand and peat mixture was necessary to eliminate the time consuming process of searching for soils with the desired SOM contents as well as the problem of separating the effects of the organic and inorganic components of soils on sorption. The microbial

population in the soil are expected to be very low owing to oven drying at 105 ^{o}C for at least 24 h followed by series of sieving, and storing at oven-dry condition in a capped plastic container (Gidda et al., 1999).

3.2.1 Soil organic matter

The SOM content of the sand and peat were measured using the loss-on-ignition method as described in literature (Leong and Tanner, 1999; Sutherland, 1998). About 5 g of soil sample was measured into a ceramic crucible and dried in an oven for 24 h at 105 ^{o}C. The sample was then ignited in a muffle furnace for 16 h at 600 ^{o}C. The analysis was performed in triplicates and the average value used. The loss of weight on ignition (LOI) was calculated by Equation [3.2] (Adam et al., 2002; Leong and Tanner, 1999; Sutherland, 1998).

$$\mathrm{LOI}(\%) = \frac{\mathrm{Weight\,at\,105^{o}\,C} - \mathrm{Weight\,at\,600^{o}C}}{\mathrm{Weight\,at\,105^{o}\,C}} * 100 \qquad [3.2]$$

Equation [3.2] gave the soil organic carbon (SOC), but was reported in this study as a measure of the SOM as suggested by Page (1982).

3.2.2 Soil water content

The soil water content was determined by gravimetric method as described elsewhere (ISO11461, 2001; Liu and Evett, 2009). About 5 g of soil sample was oven dried at 105 ^{o}C until the soil mass became stable. The mass of water in the soil sample was estimated as the difference between the wet and dry soil weights. All soil water content analyses were performed in triplicates and the average value used.

3.2.3 pH, density and porosity

The pH of the soil was measured in a 1:1 (w:w) soil:water suspension using a pH meter as described elsewhere (Ong and Lion, 1991; Page, 1982). The particle density (ρ_s) was estimated as described in Section 2.2.3.1. Dry bulk density (ρ) and porosity (n) were estimated using Equations [2.1] and [2.2], respectively. The parameters in Equations [2.1] and [2.2], such as mass and volume of soil were measured with a KERN EMB Portable balance and a 100 mL Fisherbrand calibrated cylinder, respectively.

3.2.4 Surface area and pore volume

Surface area and pore volume were measured using an Autosorb Quantachrome surface area and pore volume analyser. The surface area was estimated using the multi-point BET (Brunauer-Emmett-Teller), while the pore volume was calculated using the Barrett-Joyner-Halenda (BJH) method based on the desorption points.

3.3 Microcosm experiments

3.3.1 SOM impact experiments

All batch microcosm experiments were performed with glass vials of 60 mL (H*Ø = 140*27.5 mm) sealed with a polytetrafluoroethylene-lined cap for injection and extraction to ensure no leaks. The soils with 0, 1, 3 and 5% SOM fractions, referred to as $0\%f_{om}$, $1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$, respectively, were autoclaved by heating in an oven set at 160 ^{o}C for 16 h and thereafter wetted with hot water at 50 ^{o}C to 9% w/w similar to the moisture content used elsewhere (Höhener et al., 2006). A 65 g mass of

the wetted soils were packed into the glass vials and compacted alike by tapping vials on the worktable until stable heights were obtained. Heights in vials were 80 mm for 0%f_{om}, 84 mm for 1%f_{om}, 92 mm for 3%f_{om} and 100 mm for 5%f_{om}, leaving headspaces of 60, 56, 48, and 40 mm, respectively, in the glass vials for vapour phase sampling. The porosities were 0.45, 0.46, 0.48 and 0.48 for 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively. All experiments were performed in triplicates.

Before adding the gasoline vapours, the microcosms were stored in a Thermostatic bath/circulator (L*W*H = 52*32*21.5 cm) set at 25 ^{o}C for 24 h as shown in Figure 3.1. Then 10 mL of air was extracted from the microcosms and a 10 mL gas volume of the gasoline mixture at 25 ^{o}C were injected using a stainless steel hypodermic needle (L*Ø = 50*0.63 mm) fitted to a 10 mL gas-tight syringe. The mass of each gasoline compound in the 10 mL gas volume for the different gasoline blends, obtained by multiplying the concentration in Table 3.2 with the extracted gas volume, is summarized in Table 3.3. The decrease in concentrations of the gasoline compounds in the headspace of the microcosms was monitored daily for up to 15 days by Gas Chromatography measurements as described later in Section 3.3.4. The period of 15 days has been chosen because previous studies have shown that times of 1 h or few hours to 1 day or few days are sufficient to reach sorption equilibrium (Celis et al., 2006; Chen et al., 2007; Corseuil et al., 2004; Guo et al., 2010; Huang et al., 2003; Joo et al., 2008; Site, 2001; Wang et al., 2008a). Besides, the trial experiments conducted indicated that a period of 15 days is sufficient to reach sorption equilibrium in this study. In addition, similar experimental period has been used in previous study with gasoline (Arthurs et al., 1995). The microcosms were maintained at 25 ^{o}C in the Thermostatic bath/circulator throughout the duration of the experiment. The increase in sorption

resulting from SOM was calculated as the difference between the average sorption in SOM-containing soils and the average sorption in the 0%f_{om} soil.

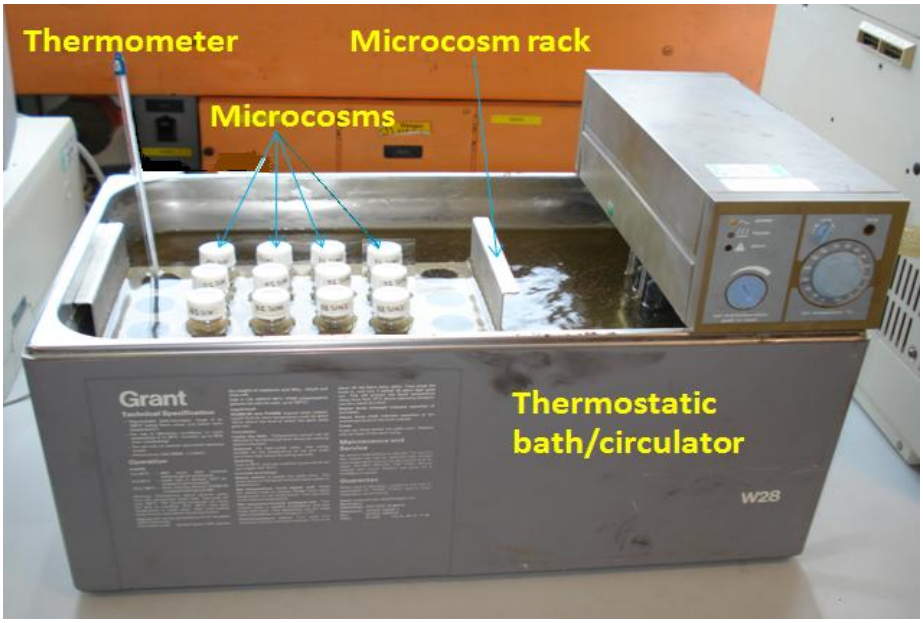

Figure 3.1 Batch microcosm experimental setups.

Table 3.3 Mass of gasoline compounds injected into microcosm.

Fuel compound	**Mass injected (g)**				
	UG	**E10**	**E20**	**B10**	**B20**
Pentane	2.43E-03	1.96E-03	1.58E-03	2.10E-03	1.81E-03
MCP	1.29E-03	1.04E-03	8.39E-04	1.12E-03	9.62E-04
MCH	6.61E-04	5.34E-04	4.29E-04	5.74E-04	4.91E-04
Benzene	1.53E-04	1.24E-04	9.84E-05	1.33E-04	1.13E-04
Toluene	1.31E-04	1.06E-04	8.51E-05	1.14E-04	9.75E-05

3.3.2 Alcohol impact experiments

The impact of alcohol on the sorption of gasoline compounds was examined by conducting similar microcosm experiments as described in Section 3.3.1

using 0%f_{om} as the soil with unblended and alcohol-blended gasoline as the contaminants individually. The impact of alcohol on the sorptive capability of SOM for gasoline compound was observed by performing similar microcosm experiments with 5%f_{om} soil using unblended and alcohol-blended gasoline and comparing the results obtained.

3.3.3 Moisture impact experiments

The effect of water content on the sorptive capacity of SOM in the soil was investigated with 5%f_{om} wetted to 0, 4.5 and 9% w/w with distilled and deionised water at 50 ^{o}C. Microcosms were similarly treated as described in Section 3.3.1. For the 0 and 4.5% w/w experiments, heights in vials were 97 and 100 mm, leaving headspaces of 43 and 40 mm, respectively. The porosities were 0.46 and 0.48 for 0 and 4.5% w/w, respectively. The height in the glass vial and the porosity of the soil for 9% w/w experiments were as described earlier in Section 3.3.1.

3.3.4 Vapour phase analysis using gas chromatography

The vapour phase concentrations of gasoline compounds in the headspace of the microcosms were analysed by injecting 40 µL of gas samples into a HR-5300 mega series Gas Chromatography (Carlo Erba, UK) equipped with a Chrompack Poraploto column (27.5m * 0.32mm * 10µm) and Flame Ionization Detector (FID). The injector was heated to 200 ^{o}C. The column temperature was held at 200 ^{o}C for 16 min (isothermal temperature program). The carrier gas was helium at a flow rate of 4 mL/min. The gasoline compounds were identified by comparing the retention time of the peaks. The peak areas were used to quantify the gasoline compounds.

Pure gasoline compounds and gasoline blends were used for the calibration of the Gas Chromatography (GC). Initially, each gasoline compound was identified by injecting 10 µL gas volume of the pure compound as well as the various gasoline blends at 25 ^{o}C into the GC using a 100 µL gas-tight syringe. Afterwards, calibration equations were obtained for all gasoline compounds by injecting 10, 30 and 50 µL gas volume of the unblended gasoline, butanol-blended gasoline and ethanol-blended gasoline into the GC.

The concentration of each gasoline compound (C_g) in the headspace vapour samples was calculated using Equation [3.3].

$$C_g = \frac{\text{Mass injected}}{\text{Volume injected}} \qquad [3.3]$$

Each gasoline compound mass was estimated using the relationship between the compound calibration equation and peak area. The calibration equations were obtained on a daily basis as shown later in Figure 4.1 in Section 4.2.2. Detailed illustrations of concentration and mass calculations are presented in Appendix A.

3.3.5 Estimation of mass distribution, sorption coefficient and retardation factor

The mass of gasoline compounds that partitioned to the soil air (M_a), soil water (M_w) and soil solid (M_s) phases of the vadose zone were estimated from the microcosm experiments using Equations [2.8], [2.9] and [2.11], respectively, as described in Section 2.4.1. The sorption coefficient (K_d) of each gasoline compound was estimated from the measured vapour

concentration as mentioned in Section 2.4.2.1 using Equation [2.12 or 2.15]. By using Equation [2.15], the K_d of each gasoline compound at 0% w/w was reasonably estimated. More so, since the effect of alcohol on gasoline compounds would be significant only at the very early spill times due to the ease of alcohol partitioning to the soil water (Powers et al., 2001b; Reckhorn et al., 2001), the average K_d of all daily K_d was used in this work in order to capture the complete effect of alcohol on gasoline compounds following release. The retardation factor (R) of each gasoline compound was estimated using Equation [2.16] as described in Section 2.4.2.2. Calculated examples of M_a, M_w, M_s, K_d and R are provided in Appendix A.

3.4 Mini-lysimeter experiments

3.4.1 Design of mini-lysimeter

A section view of the mini-lysimeter used in this research is shown in Figure 3.2. The mini-lysimeter was designed to a dimension of 14 cm internal diameter by 40 cm height, and constructed using a transparent Perspex plastic tube of 0.5 cm thickness. The 14 cm x 40 cm dimension was chosen because it makes a midway size system between the systems used in the field and those used in the laboratory, and can be suitably managed as discussed in Section 2.5.3. Perspex was chosen because it is transparent, light, easily workable, cheap and not fragile, and does not rust or react with the contaminants under investigation.

The mini-lysimeter was equipped with 8 sampling ports, 2 injection ports, 1 groundwater outlet tube and a lid. The sampling ports were made of stainless steel tube of 4 mm internal diameter, 6 mm external diameter

and 21 cm length, with 1 mm diameter perforations at 1 cm interval across the 14 cm length inside the Perspex plastic tube. They were strategically positioned along the mini-lysimeter height to closely monitor the migration of contaminant within the system. Stainless steel was chosen because it does not rust or react with the contaminants under investigation and will remain perfectly horizontal at the designated position. The injection ports were made of stainless steel tube of 4 mm internal diameter, 6 mm external diameter and 14 cm length, having the outer end curved upward to a height of 6 cm for easy injection of contaminant. The injection ports were located at 9 and 23 cm to simulate surface spills and subsurface leaks, respectively. The groundwater outlet tube was made of a Perspex tube of 4 mm internal diameter, 6 mm external diameter, 27 cm length, and was positioned at the bottom of the mini-lysimeter. Attached to the mini-lysimeter's lid was a rain simulator made of Perspex with a 13 cm external diameter and 1.3 cm external thickness, a 10 cm internal diameter and 1 cm internal depth, with a 0.5 mm diameter perforations across the internal base. The mini-lysimeter's lid and base were made of Perspex of 1.5 cm and 5 cm thickness, respectively.

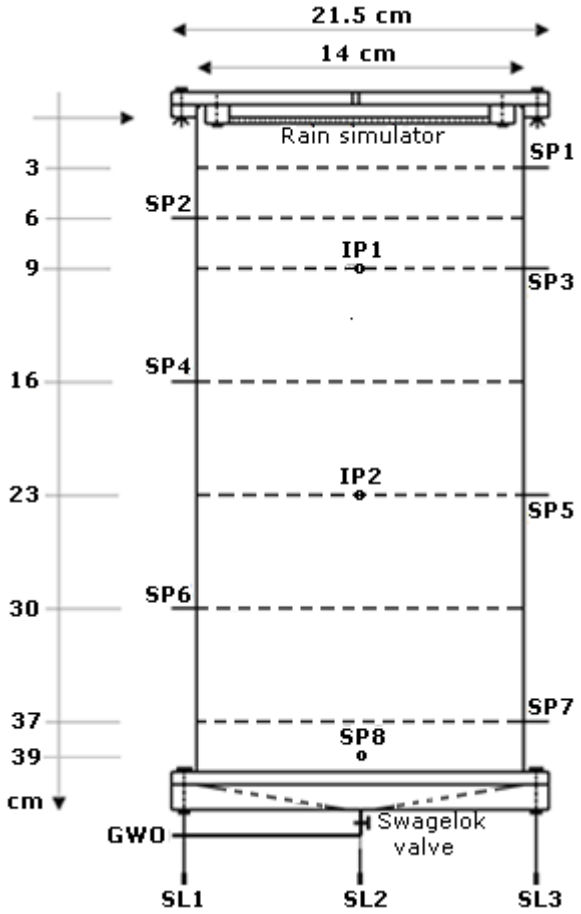

Figure 3.2 A section view of the mini-lysimeter.

(SP1 – SP8 are sampling ports; IP1 & IP2 are injection ports; GWO is the groundwater outlet tube; and SL1 – SL3 are supporting legs).

3.4.2 Loading the mini-lysimeter with soil

The loading of soil into the mini-lysimeter is shown in Figure 3.3a - c. All soil components were sterilised as described in Section 3.3.1 to prevent biological processes taking place. A 3 cm depth layer of uncontaminated fine gravels, obtained from Nottingham (UK), was placed in the bottom and uniformly levelled (Figure 3.3a). The mini-lysimeter was then packed with dry uncontaminated sand mixed with 0 – 5% SOM (≈4308.08 cm^3) to a height of 31 cm (Figure 3.3b). The remaining 9 cm void of the mini-

lysimeter served as the headspace. The mini-lysimeter was carefully capped and the soil wetted via the rain simulator, with 1.8 L of distilled and deionised water, until water began to flow via the groundwater outlet tube aligned to the bottom of the vadose zone at exactly 28 cm from the soil surface (Figure 3.3c). The excess water that accumulated at the bottom of the mini-lysimeters was later drained by lowering the groundwater outlet tube, thus allowing a large number of the soil pores to be filled with gas (Page, 1982). The mini-lysimeter was left for 2 days for the soil to stabilize and maintain residual water saturation that simulated vadose zone soil at field capacity moisture condition (Österreicher-Cunha et al., 2009). No further soil wetting was performed throughout the duration of the experiment, hence, mimicking non-rainy soil condition with no bacterial activity. Consequently, the water phase in the soil was considered immobile.

Prior to contamination on the third day, the mini-lysimeter's sampling and injection ports and groundwater outlet were closed and the background concentrations of gasoline compounds in the soil gas were measured. Thereafter, the mini-lysimeter was uncapped and 400 g of dry soil contaminated with 10 mL alcohol/gasoline blends placed on the soil surface to simulate a surface spill following the method used by Pasteris et al. (2002) in their lysimeter experiment as discussed in Section 2.5.2.1. The mini-lysimeter was quickly capped after the placement to maintain a closed system. According to Pasteris et al. (2002), the 10 mL alcohol/gasoline blends should fill 2% of the total porosity of the soil. This percentage was within the 1 - 7% of the pore space usually occupied by gasoline residual in the vadose zone after spills (see Section 2.4.3.1). Hence, migration of gasoline compounds in the liquid phase (NAPL or dissolved phase) should not occur during this experiment. The contaminated mass of soil served as

the contamination source zone. The mini-lysimeter was maintained at a temperature of 25 ^{o}C throughout the experiment. A vertical experimental system such as mini-lysimeter has been chosen and used in this study because it simulates both the vadose zone and the underlying groundwater zone, hence, enabled the investigation and estimation of the extent of groundwater contamination by ethanol-blended and butanol-blended gasoline compounds after release.

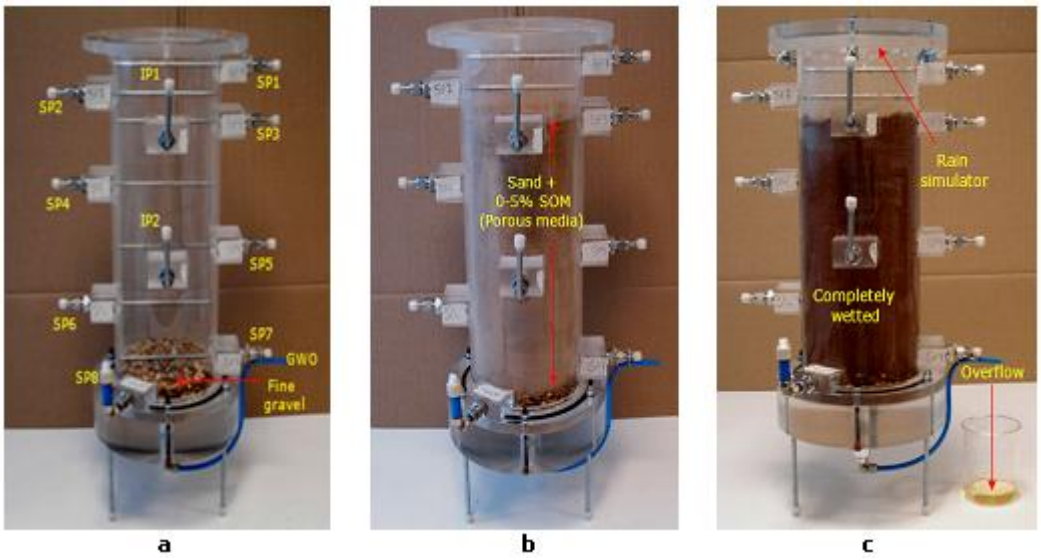

Figure 3.3 Stepwise setup of mini-lysimeter: (a) emplacement of uncontaminated fine gravel, (b) emplacement of uncontaminated dry soil and (c) wetting of soil.

3.4.3 Alcohol impact experiments

Experiments to determine the effect of alcohol on the vapour phase transport of gasoline compounds in the vadose zone were setup as described in Section 3.4.2 using 0%f_{om} as the soil. The alcohol/gasoline blends used were E0 - E20 for the ethanol-blended gasoline experiments and B0 - B20 for the butanol-blended gasoline experiments.

3.4.4 SOM impact experiments

To determine the impact of SOM on the vapour phase transport of alcohol-blended gasoline compounds in the vadose zone, the mini-lysimeter was setup with 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om}, and contaminated with UG, E20 and B20, respectively. The results obtained were compared for the different SOM fractions and the different gasoline blends. The choice of 20% alcohol was motivated by the consistent increase of ethanol volume in gasoline as mentioned earlier in Section 3.1 and thus would make a good representation of future gasoline blend.

3.4.5 Soil gas sampling and analysis

Before contamination, soil gas samples were extracted from SP1 (headspace), SP3 – SP7 (vadose zone) and SP8 (groundwater zone) and analysed for background concentrations of gasoline compounds (see Figures 3.2 and 3.3). Immediately after contamination, the source zone (SP3) was sampled and analysed, and the concentration obtained was used as the initial concentration of gasoline compounds. Thereafter, soil gas samples were extracted from the source zone as well as from the other sampling ports to monitor changes in the concentrations of gasoline compounds. Soil gas samples were extracted after 4 h (Day 1) and daily from Days 2 to 15. The soil gas samples were extracted and analysed by HPR-20 Mass Spectrometer (MS) as shown in Figure 3.4 to obtain real-time data. The HPR-20 Mass Spectrometer (Hiden Analytical, England) was equipped with Capillary, Quadrupole Mass Analyser (HAL 201-RC) and Faraday & Secondary Electron Multiplier (SEM) Detectors and used a MASsoft version of 6.13.0.35 and a Micro board of type HAL 5. The MS was set to use the SEM Detector for faster scanning at a voltage of 850V. The MS scan was configured to Multiple Ion Detection (MID) to simultaneously

measure compounds of different masses. Other MS settings included source emission of 100 μA, mass range of 0.40 to 200 amu at a minimum increment of 0.01 amu, and acquisition range of 10^{-8} to 10^{-13} torr for all compounds. Soil gas samples were extracted automatically via the capillary heated up to 200 ^{o}C to improve condensable species sampling. The MS was operated at a normal vacuum pressure of ≈1 x 10^{-6} torr. Each port was sampled for 20 min to obtain a stable partial pressure values. A total soil gas volume of 16 mL was extracted per sampling time. The concentration of each gasoline compound was calculated from the average of the last three stable partial pressure values using a partial pressure-concentration relationship developed for each compound and each gasoline blend during the MS calibration as suggested in Section 2.6.2. The partial pressure-concentration relationship for the individual gasoline compounds for the different gasoline blends is presented later in Table 4.3 in Section 4.3.4 and its application in concentration calculation is illustrated in Appendix A.

Figure 3.4 Soil gas sampling and analysis using HPR-20 Mass Spectrometer.

3.4.6 Water retention capacity and infiltration rate

The water retention capacities of the soils at dry and field capacity moisture conditions (see Section 2.2.3.6) were measured by releasing known volume of water via the rain simulator and measuring the volume of water drained via the groundwater outlet. The volume of water retained by soils was estimated as the difference between the volume of water released and the volume of water drained. The soil water retention capacity (WRC) was then estimated as a simple ratio of the volume of water retained to the volume of soil as expressed in Equation [3.4].

$$\text{WRC} = \frac{\text{Volume of water retained by soil}}{\text{Volume of soil}} \qquad [3.4]$$

The mass of water retained at the different sections of the soil was determined by gravimetric method as described in Section 3.2.2. The volume of water retained, θ_v, at the different sections of the soil was then calculated using Equation [2.5].

$$\theta_v = \frac{\text{volume of water}}{\text{bulk volume of soil}} = \frac{(\text{mass of water/density of water})}{\text{sample volume}}$$

The water infiltration rates in the soil were measured by releasing known volumes of water via the rain simulator and observing how long it took to reach the gravel aquifer following the discussion in Section 2.4.3.1. The start of drainage at the groundwater outlet indicated the time the released water arrived at the saturated zone. The infiltration rate of water in the soil was calculated using Equation [3.5].

$$\text{Water infiltration rate} = \frac{\text{Distance infiltrated (28 cm)}}{\text{Time taken}} \qquad [3.5]$$

CHAPTER FOUR

4. BASELINE MEASUREMENTS

4.1 Introduction

This chapter provides a detailed explanation of how the data used in this study were generated. It starts by establishing the baseline detection of gasoline compounds by the various sets of equipment based on how the samples were extracted. It concludes by presenting the baseline measurements describing the changes in soil properties with SOM addition, and the implication of such changes with regards to soil and groundwater contaminations.

4.2 Compound identification baseline

4.2.1 Compound identification with Gas Chromatography

Each synthetic gasoline compound in the various gasoline blends was identified as described in Section 3.3.4. The retention time for each pure gasoline compound was used to identify the gasoline compounds in the various gasoline blends as explained in Section 3.3.4. Table 4.1 summarises the retention time for each gasoline compound both in pure state and in gasoline blends. Generally, the retention time of all gasoline compounds was lower in the pure state than in the mixed state. Among the mixed state, retention time was generally in the order of UG<B20<E20. This change in retention time between the pure and mixed states and among the mixed states indicates change in individual gasoline compound characteristics due to interactions with other gasoline compounds. This supports the hypothesis in Section 1.1 that the mixing of hydrocarbons to

form gasoline will promote intermolecular interactions amongst the gasoline compounds and that the addition of alcohol to the gasoline will further impact the intermolecular interactions amongst the gasoline compounds. Therefore, the data indicate that a single hydrocarbon is unlikely to represent gasoline and that the addition of alcohol to gasoline could impact the behaviour of the gasoline compounds. The data also indicate that ethanol and butanol may have different degree of impacts on the behaviour of gasoline compounds.

Table 4.1 GC-FID retention time of gasoline compounds in different blends.

Gasoline compound	**Retention time, min**			
	Pure compound	**UG**	**B20**	**E20**
Ethanol	1.93	-	-	2.07
Pentane	2.30	2.38	2.39	2.46
MCP	3.61	3.69	3.72	3.93
Benzene	4.15	4.35	4.34	4.61
Butanol	4.76	-	4.77	-
MCH	6.17	6.29	6.30	6.70
Toluene	7.27	7.56	7.52	8.02
Octane	9.82	10.23	10.08	10.70

4.2.2 Gas Chromatography calibration

Having identified each gasoline compound, the GC-FID was calibrated as described in Section 3.3.4. The peak areas obtained from the injections were plotted against the mass injected to obtain calibration equations. The calibration equation for each gasoline compound was used to calculate the mass of that compound from experimental headspace samples. Figure 4.1 shows typical calibration plots and equations for pentane in E20, B20 and UG. The calibration equation for E20-pentane contained a higher value

compared with B20-pentane and UG-pentane. The regression coefficient (R^2) was least for E20-pentane and highest for UG-pentane. These calibration plots and equations indicate that ethanol may have greater impact on the behaviour of gasoline compounds than butanol.

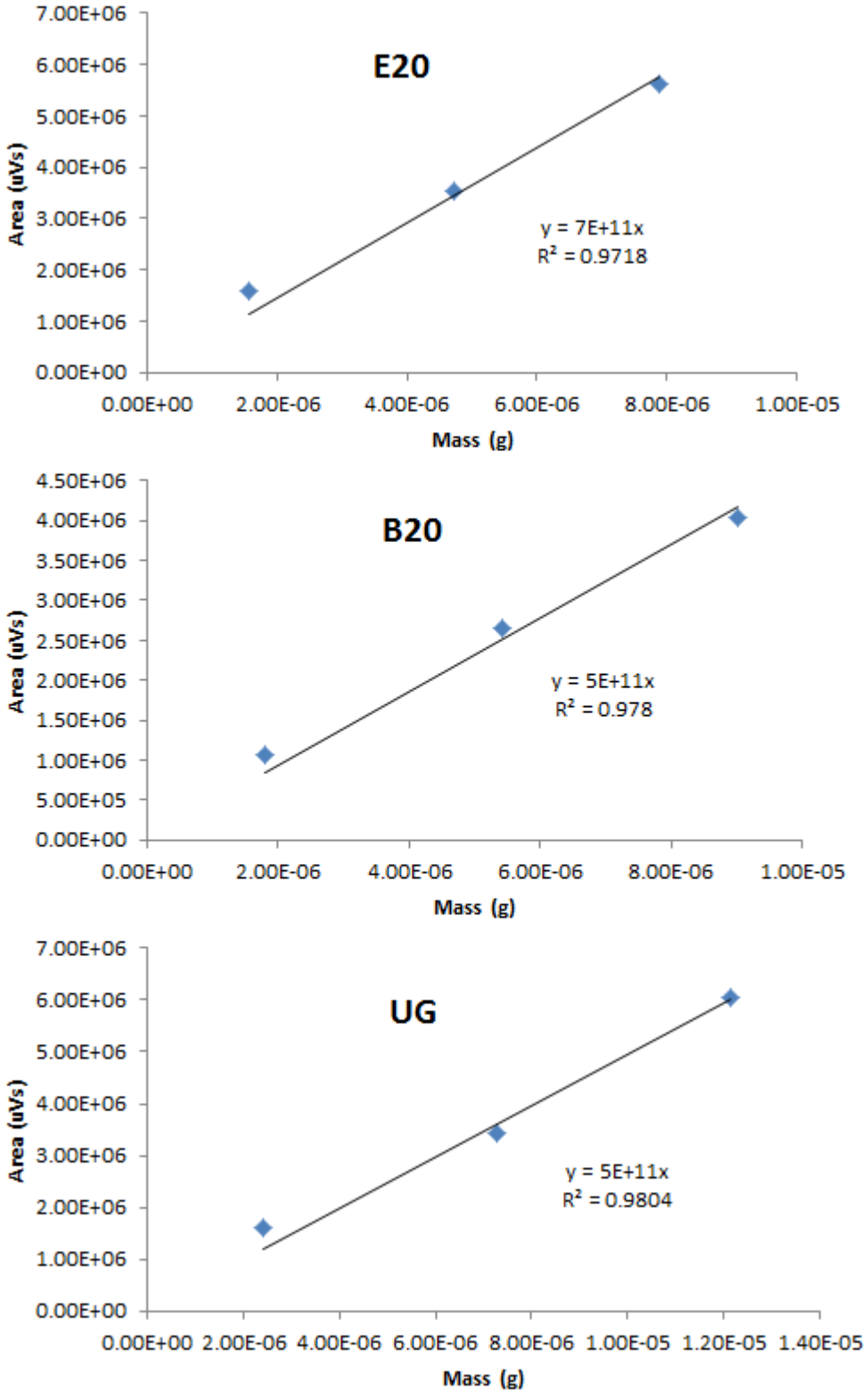

Figure 4.1 Typical calibration plots and equations for pentane in E20, B20 and UG.

4.2.3 Compound identification with Mass Spectrometer

All the synthetic gasoline compounds were "fingerprinted" by creating two files that recognized each compound with a unique mass and ionization profile at chosen percentages that reduced overlaps to a minimum as illustrated in Table 4.2a - b. The files were installed and the Mass Spectrometer operated as described in Section 3.4.5. File 1 was created for the ethanol-blended gasoline (Table 4.2a), while File 2 was for the butanol-blended gasoline (Table 4.2b). The bold numbers in both files are masses, ranging from the lightest to the heaviest compound used. The numbers below the masses are percentages of the respective compounds that could be found under the individual masses. The pink-coloured percentages are percentages with high overlaps, while the blue-coloured are percentages with the least possible overlaps. The blue-coloured percentages were chosen for the respective compounds, and the masses under which they appeared were the unique masses used to identify the respective compounds. Accordingly, pentane was identified with a unique ionization mass of 72, octane with 71, MCP with 69, MCH with 83, benzene with 78, toluene with 91, and ethanol (File 1) and butanol (File 2) both with 31.

Table 4.2 Individual gasoline compound unique mass distribution key used for MS identification (a) File 1 for ethanol-blended gasoline and (b) File 2 for butanol-blended gasoline.

(a)

File 1	Mass										
	16	**31**	**32**	**43**	**56**	**69**	**71**	**72**	**78**	**83**	**91**
Pentane				100	4.2		1	13			
Octane				100	18.5		20.3	1			
MCP				8.3	100	36					
MCH				7.4	28.6	23.1	1.8			100	
Benzene									100		
Toluene											100
Ethanol		100		11							

(b)

File 2	Mass										
	16	**31**	**32**	**43**	**56**	**69**	**71**	**72**	**78**	**83**	**91**
Pentane				100	4.2		1	13			
Octane				100	18.5		20.3	1			
MCP				8.3	100	36					
MCH				7.4	28.6	23.1	1.8			100	
Benzene									100		
Toluene											100
Butanol	0.36	98	2.2	68	100						

4.2.4 Mass Spectrometer calibration

The files created from Section 4.2.3 were installed in the MS and used to analyse vapours in the headspace of glass vials containing UG, B0 to B20 and E0 to E20. From the partial pressures obtained and the known vapour phase concentrations of each gasoline compound in the different gasoline blends (see Table 3.2 in Section 3.1), a relationship between partial pressure and concentration was developed for each gasoline compound and for each gasoline blend. Table 4.3 summarises the concentration equivalent

of the partial pressure for each gasoline compound for the different gasoline blends used. The concentration equivalent of the partial pressure for UG was quite different from the alcohol blends. Among the alcohol blends, the concentration equivalent of the partial pressure for all gasoline compounds generally decreased with increasing alcohol volume in gasoline. More so, the concentration equivalent of the partial pressure for the gasoline compounds was generally greater for the butanol blends compared with the ethanol blends. Therefore, the data suggest that alcohol may impact the behaviour of gasoline compounds, and that ethanol and butanol are likely to have different degree of impacts.

Table 4.3 Concentration equivalent of 1 torr of gasoline compounds obtained from MS for different gasoline blends.

Compd.	**UG**	**B10**	**B20**	**E10**	**E20**
	g/mL	**g/mL**	**g/mL**	**g/mL**	**g/mL**
Pentane	9.83E+04	4.71E+05	1.37E+05	3.36E+05	8.34E+04
Octane	8.02E+04	1.61E+05	9.84E+04	1.19E+05	4.96E+04
MCP	6.05E+04	1.57E+05	6.94E+04	1.16E+05	2.90E+04
MCH	1.84E+05	2.21E+05	9.94E+04	1.43E+05	2.08E+04
Benzene	2.42E+04	6.26E+04	3.03E+04	5.42E+04	1.44E+04
Toluene	3.76E+05	2.41E+05	2.58E+05	1.76E+05	1.46E+05
Butanol	-	5.47E+03	8.13E+03	-	-
Ethanol	-	-	-	2.30E+03	2.84E+03

4.3 Analysis of soils

Table 4.4 summarises the soil analysis results. The pH of the soil gradually changed from alkaline to slightly acidic as the fraction of the SOM was increased, suggesting that the SOM source was acidic. As discussed in Section 2.2.3.7, the addition of SOM to a soil altered the soil physical and

chemical properties. This is clearly reflected in this analysis by the increasing surface area, porosity and total pore volume of sand with increasing SOM fraction. As expected, particle density decreased with increasing SOM due to the lesser weight of SOM compared with an equal volume of inorganic solids (Section 2.2.3.1). Also, the bulk density of the soil decreased with increasing SOM due to the poor packing of SOM particles compared with those of sand (Section 2.2.3.4). Generally, this soil analysis indicated that the addition of SOM to sand changed the conformation of the soil to lower pH, higher porosity and greater surface area, hence is likely to increase the sorption capability of the soil.

Table 4.4 Soil composition and characterisation.

Soil	**Description**	**Properties**					
		pH	**ρ_s**	**ρ**	**n**	**SA**	**TPV**
		-	**g/mL**	**g/mL**	**-**	**m^2/g**	**cm^3/g**
$0\%f_{om}$	Sand + 0%SOM	9.10	2.5	1.22	0.51	0.82	4.04E-3
$1\%f_{om}$	Sand + 1%SOM	8.51	2.4	1.17	0.52	1.04	4.47E-3
$3\%f_{om}$	Sand + 3%SOM	7.34	2.3	1.07	0.53	1.47	5.33E-3
$5\%f_{om}$	Sand + 5%SOM	6.17	2.1	0.97	0.54	1.91	6.20E-3

ρ_s = Particle density; ρ = Bulk density; n = Porosity; SA = Surface area; TPV = Total pore volume

4.4 Changes in soil properties with SOM addition using mini-lysimeter

4.4.1 Changes in water retention capacity

The water retention capacities (WRCs) of all soils used were measured at both oven dry (OD) and field capacity (FC) moisture conditions using the mini-lysimeter and the results obtained are shown in Figures 4.2 and 4.3, respectively. The OD and FC moisture conditions represent the water content at the soil surface and the lower section of the vadose zone,

respectively (Section 2.2.3.6). The water retention capacity increased with increasing SOM fraction (f_{om}) of the soil at both OD and FC moisture conditions (Figure 4.2), confirming the already established high water absorption capacity of SOM (Page, 1982). This effect was, however, greater at FC than at OD moisture condition. At OD moisture condition, the WRC of the soils increased by 2.2%, 9.9% and 15.2% for 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively. While at FC, the increase was 11.5%, 53.9% and 73.1% for 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively. As expected, the water absorption capacity for all soils was high at OD, hence, resulting in little difference in WRC among the soils. On the contrary, the water absorption capacity for all soils was low at FC and solely controlled by SOM, which is probably the reason for the higher difference in WRC among soils with varying SOM fractions.

The mini-lysimeter experiments with fuel contamination in Chapters 5 to 7 were performed at FC, which is the water content commonly found in the subsurface environment (Section 2.2.3.6). Figure 4.3 shows that the volumetric water content of all soils increased linearly from the soil surface to the soil base at 28 cm depth under this condition. The volumetric water content ranged from 11% at the soil surface to 24% at the base for 0%f_{om}, while it was 12% to 25% for 1%f_{om}, 14% to 27% for 3%f_{om}, and 16% to 30% for 5%f_{om}. Similar water content variation at field capacity for sorbents with varying SOM contents has been reported (Ong and Lion, 1991). Also, Pasteris et al. (2002) have reported similar observation for a large scale lysimeter experiment. Therefore, based on these WRC results obtained, it could be reasonable to state that the mini-lysimeter can closely simulate the subsurface environment.

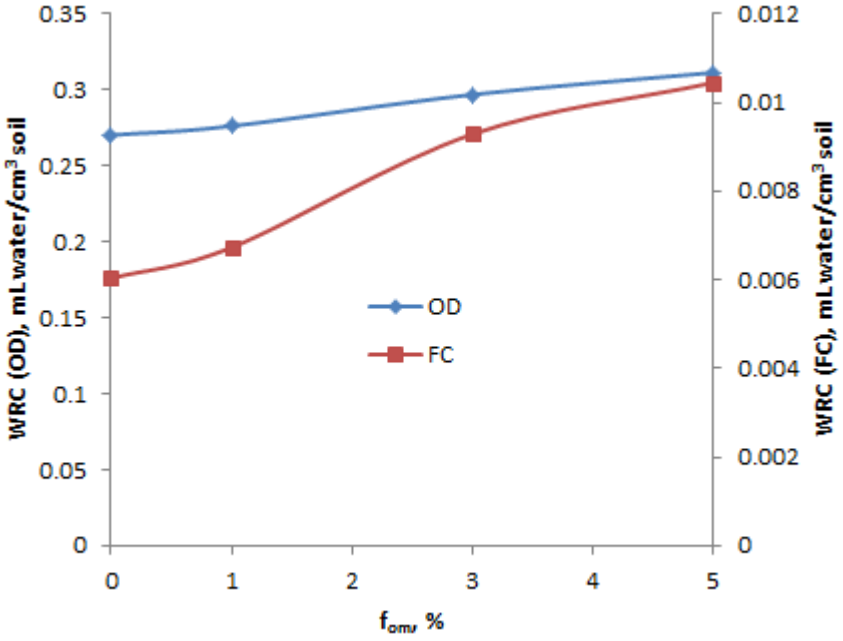

Figure 4.2 Water retention capacity (WRC) of soils as a function of SOM fraction and moisture condition.

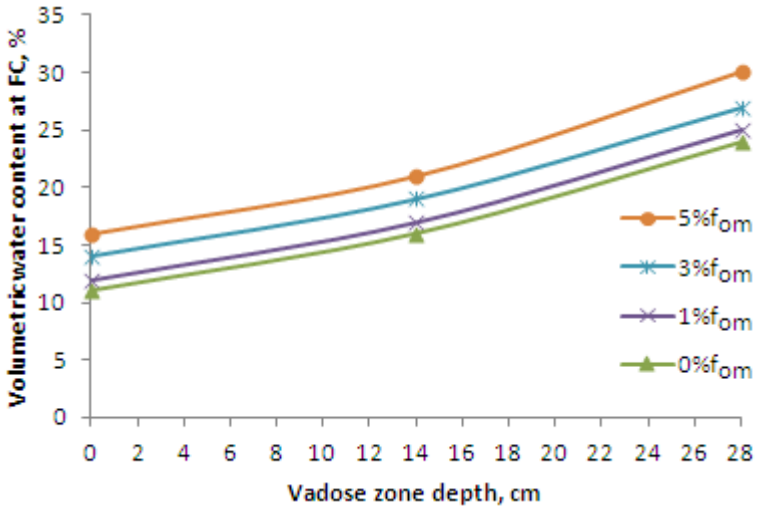

Figure 4.3 Volumetric water content of soils at field capacity (FC) as a function of depth and SOM fraction.

4.4.2 Changes in water infiltration rate

Figure 4.4 shows the results of the water infiltration rates (WIRs) of the soils used as a function of moisture content and SOM fraction as described

in Section 3.4.6. The WIR in the soils changed with increasing SOM fraction (f_{om}) at different moisture conditions. At OD moisture condition, the WIR in the soils decreased with increasing f_{om}, while at FC it increased with increasing f_{om}. The decrease in WIR with increasing f_{om} at OD moisture condition could be due to the high water absorption capacity of SOM, as more water will be required to saturate the soil grains as a prerequisite to water infiltration. Also, the SOM will swell due to water uptake which may change porosity. However, at FC, the soil grains are already or nearly saturated. Hence, water infiltration will be dependent on the soil overall porosity. According to Page (1982) and Serrano and Gallego (2006), SOM plays an important role in the improvement of soil porosity. Therefore, it implies that the addition of SOM may have improved the connectivity of the pores in the soil at FC, possibly due to the swelling of the SOM. This improved connectivity of pores could be the possible reason for the observed increase in the WIR with increasing f_{om}.

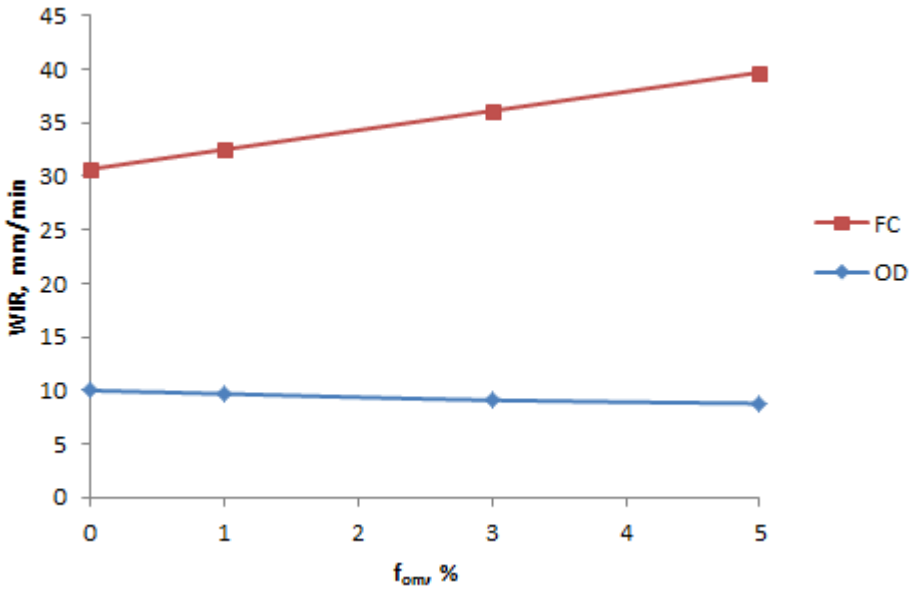

Figure 4.4 Water infiltration rates of soils as a function of SOM content and moisture condition.

Another interesting observation was the increase in WIR with increasing volume of water released at FC in Figure 4.5. The WIR increased with increasing volume of water released until an upper limit of 400 mL was reached when the WIR remained constant despite the increase in water volume from 400 to 600 mL. This result suggests that at a certain volume range, the volume of contaminant released will be a dominant factor determining the degree of groundwater contamination. However, above such volume range, the contribution of contaminant volume will stabilize and other factors, such as the geologic properties of the contaminated site (see Section 2.4.3), will be more responsible for any variation in the degree of groundwater contamination.

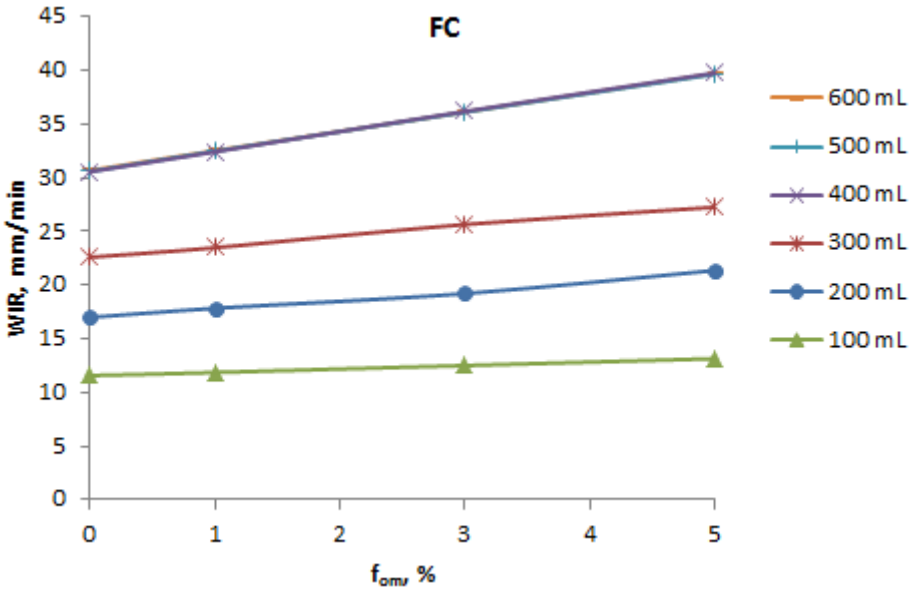

Figure 4.5 Water infiltration rate of soils at field capacity as a function of SOM content and volume of water released.

4.5 Sorption of unblended gasoline by soils at OD and FC moisture conditions using microcosm

4.5.1 Headspace concentration of gasoline compounds

Figure 4.6 shows the headspace vapour concentrations of representative UG gasoline compounds for sandy soil (0%f_{om}) and sandy soil mixed with 5% SOM (5%f_{om}) at OD (0% w/w), FC (9% w/w) and midway (4.5% w/w) moisture conditions found from Section 4.4.1 using the microcosm (Section 3.3.3). The increase in soil water content generally caused an increase in the headspace concentrations of UG gasoline compounds, indicating decrease in the sorption of gasoline compounds by the soils. This decrease in sorption has been interpreted to be due to the blockage of some of the sorption sites of the soils (Section 2.2.3.6). The presence of SOM generally reduced the impact of water content on sorption by more than 30% for pentane and more than 60% for MCP and benzene. This indicates that the contribution of SOM to sorption could be significant at field capacity.

At OD moisture condition, a complete disappearance of benzene, representing the aromatic compounds, was observed six days after contamination, while the representatives of the alkanes and cycloalkanes (Pentane and MCP, respectively) persisted at the headspace at negligible concentrations throughout the 15 days duration of the experiment. The percentages of pentane and MCP at the headspace on Day 15 ranged from 0.1% for 5%f_{om} to 0.2% for 0%f_{om}, respectively. At midway and FC moisture conditions, no complete disappearance was observed for any gasoline compounds at the headspace throughout the experimental period. The percentages of the gasoline compounds at the headspace on Day 15 for midway moisture condition ranged from 3.5% (5%f_{om}) to 6.0% (0%f_{om}) for pentane, from 2.0% (5%f_{om}) to 5.4% (0%f_{om}) for MCP and from 0.6%

(5%f_{om}) to 1.5% (0%f_{om}) for benzene. In contrast, the percentages of the gasoline compounds at the headspace on Day 15 for FC moisture condition ranged from 5.2% (5%f_{om}) to 8.9% (0%f_{om}) for pentane, from 3.0% (5%f_{om}) to 8.3% (0%f_{om}) for MCP and from 0.8% (5%f_{om}) to 1.9% (0%f_{om}) for benzene. This result clearly shows that the sorptive capability of soil could be reduced with increasing soil water content, thus indicating that the degree of gasoline retention by a soil may differ with seasons. The data also indicate that the SOM content of soils could contribute significantly to sorption in wet conditions and when alcohols are added.

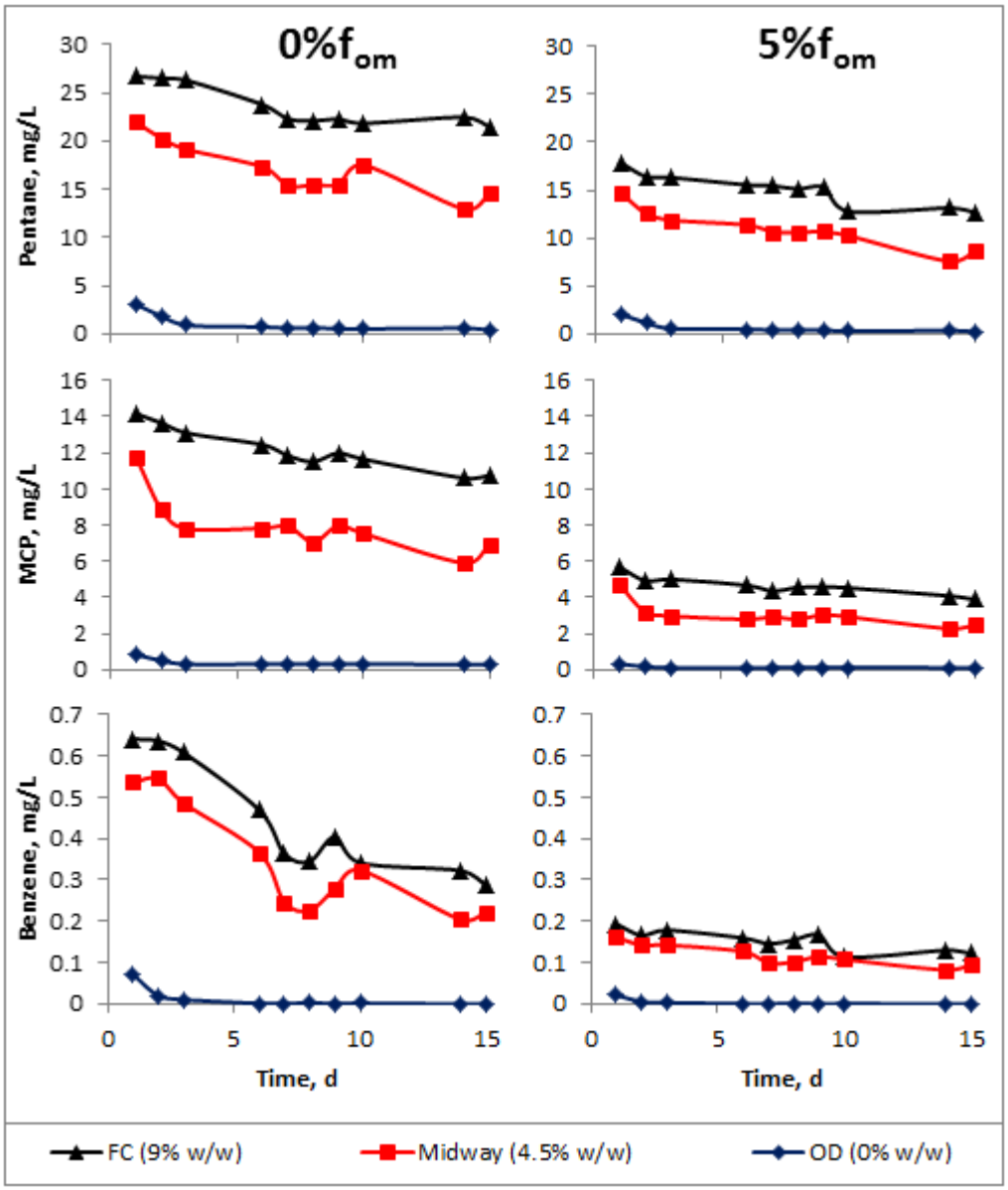

Figure 4.6 Headspace concentrations of gasoline compounds with time as a function of soil water and SOM contents.

4.5.2 Sorption coefficient of gasoline compounds

Figure 4.7 shows the average sorption coefficient (K_d) values for UG gasoline compounds with changing soil water content of sandy soil ($0\%f_{om}$) and sandy soil mixed with 5% SOM ($5\%f_{om}$). The K_d values for UG gasoline compounds generally decreased with increasing soil water content, implying a decrease in adsorption on the soil solids or increase in

partitioning to the soil water. The decrease in K_d was generally about 50% less for 5%f_{om} than for 0%f_{om}, suggesting that SOM can significantly improve the adsorption of contaminants at different moisture conditions. Similar decrease in the K_d values for trichloroethylene vapour with increasing soil water content for different soils has been reported (Ong and Lion, 1991). Since an increase in the surface area (SA) of soils is known to increase the K_d of gasoline compounds (see Section 2.2.3.3), it means that the observed decrease in the K_d values for the UG gasoline compounds with increasing soil water content could be due to the reduction in the SA of the soil as also noted in Section 2.2.3.6. The K_d values for gasoline compounds at the tested moisture conditions are scarce in the literature. However, the K_d values obtained at FC moisture condition for 0%f_{om}, 57.8 L/kg for pentane, 17.3 L/kg for MCP and 1.1 L/kg for benzene, were approximately one order higher than those reported for sandy soil, e.g. 4.4 L/kg for pentane, 1.7 L/kg for MCP (Pasteris et al., 2002) and 0.2 L/kg for benzene (Joo et al., 2008). The difference in the K_d values can be attributed to the moisture condition and the particle size of the sand used. For example, Joo et al. (2008) used a soil-to-water ratio of 1:2 (w/w) which is obviously higher than the FC (9% w/w) used in this study. Also, Pasteris et al. (2002) used coarse sand, which contrasts to the fine sand used in this study. As discussed in Chapter 2, K_d values for contaminants are likely to decrease with increasing soil water content (Section 2.2.3.6) and likely to increase with decreasing soil particle size (Section 2.2.3.2). Therefore, the higher K_d values for gasoline compounds obtained in this study as compared to those reported in literature was expected. Overall, the data indicate that soil water content is an important soil property that can influence the adsorption and partitioning processes of contaminants following release to the soil.

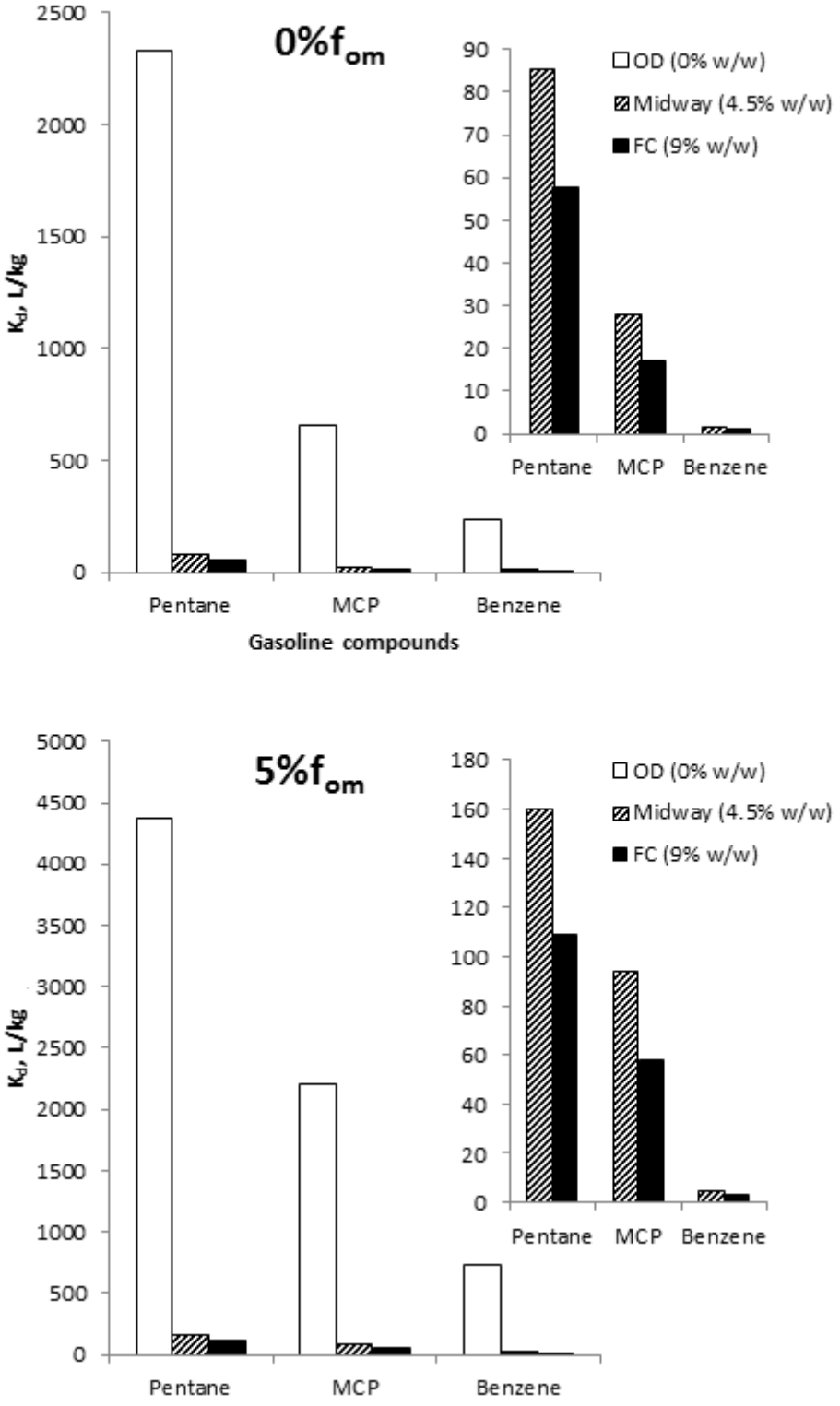

Figure 4.7 Average sorption coefficient (K_d) of gasoline compounds as a function of soil water and SOM contents.

CHAPTER FIVE

5. IMPACT OF SOM ON THE SORPTION AND TRANSPORT OF ETHANOL-BLENDED GASOLINE VAPOURS IN THE VADOSE ZONE

5.1 Introduction

The sorption and transport of contaminants in the vadose zone determines the volume of contaminants that migrate to the groundwater after a spill to the vadose zone. Previous studies have shown that the SOM in soils can impact the sorption and transport of contaminants in the vadose zone (Section 2.2.3.7). Until now, it is still unclear how SOM will affect the sorption and transport of complex mixtures, such as E0 - E20, in the vadose zone. To gain this understanding, a series of microcosm and mini-lysimeter experiments were conducted (see Sections 3.3 and 3.4, respectively). While E0, E10 and E20 were collectively used to illustrate the impact of ethanol on the sorption and transport of gasoline compounds in the vadose zone, the study on the impact of SOM focused on E20, which represents future gasoline blend, especially for U.S and UK. The choice of E20 was motivated by the consistent increase of ethanol volume in gasoline as mentioned earlier in Section 3.1.

5.2 Microcosm experiments

5.2.1 Impact of ethanol on the sorption and phase distribution of gasoline compounds

5.2.1.1 Sorption of gasoline compounds

Figure 5.1 compares the headspace concentrations of the gasoline compounds with time as a function of gasoline composition after injection as described in Section 3.3.2. Octane, the second alkane in the synthetic gasoline mixture, was not included in Figure 5.1 due to poor detection by the GC-FID used for the headspace vapour sample analysis (see Appendix B). All experiments were conducted with normal sand (0%f_{om}) to eliminate the interference by SOM and to illustrate the worst case scenario on the environmental impact of ethanol-blended gasoline on subsurface environment (Adam et al., 2002). The headspace concentrations of all the gasoline compounds decreased with time due to increase in sorption. Biodegradation did not occur due to the thorough autoclaving of the soil prior to experiment. The addition of ethanol to gasoline reduced the sorption of all gasoline compounds, probably due to the early high ethanol sorption and the associated blockage of the soil sorption sites. This reduction suggests that the use of ethanol-blended gasoline as a transportation fuel could result in greater groundwater contamination with gasoline compounds. Similar reduction in contaminants sorption in the presence of ethanol has been reported (Adam et al., 2002; Powers and McDowell, 2001). The reduction in the sorption of ethanol-blended gasoline compounds was generally greatest on Day 1, implying that the increase in groundwater contamination with ethanol-blended gasoline will be greatest during the first day of a spill. Similar observation has been reported for E26 and M85 (85% methanol blend) gasoline compounds (Powers et al.,

2001b; Reckhorn et al., 2001). These studies noted that the presence of ethanol would have a significant effect on gasoline compounds only at very early leaching times when ethanol still persist and thereafter would have insignificant effect due to ethanol wash out and/or biodegradation. Figure 5.1 shows that the effect of ethanol on the sorption of gasoline compounds was significant between Days 1 and 6 as ethanol persisted in the headspace, but insignificant between Days 6 and 15 due to the partitioning of the ethanol to the soil water. Among the gasoline compounds, the sorption of the aromatics was reduced to a greater extent of above 90% than those of the cycloalkanes of 25 – 52% and the alkanes of only 28%. For benzene, the aromatics representative, the effect persisted even when sorption equilibrium had been reached for E20. This is particularly of great concern because, as noted in Section 2.3.2, the adverse health effects associated with the exposure of gasoline are due to the presence of the aromatics. Therefore, the addition of 20% ethanol by volume to gasoline in attempts to reduce vehicular emissions to the atmosphere could have detrimental effect on the groundwater. The data clearly show that the addition of ethanol to gasoline could reduce the sorption of gasoline compounds, and increasing the volume of ethanol in gasoline would result in further reduction in the sorption of gasoline compounds.

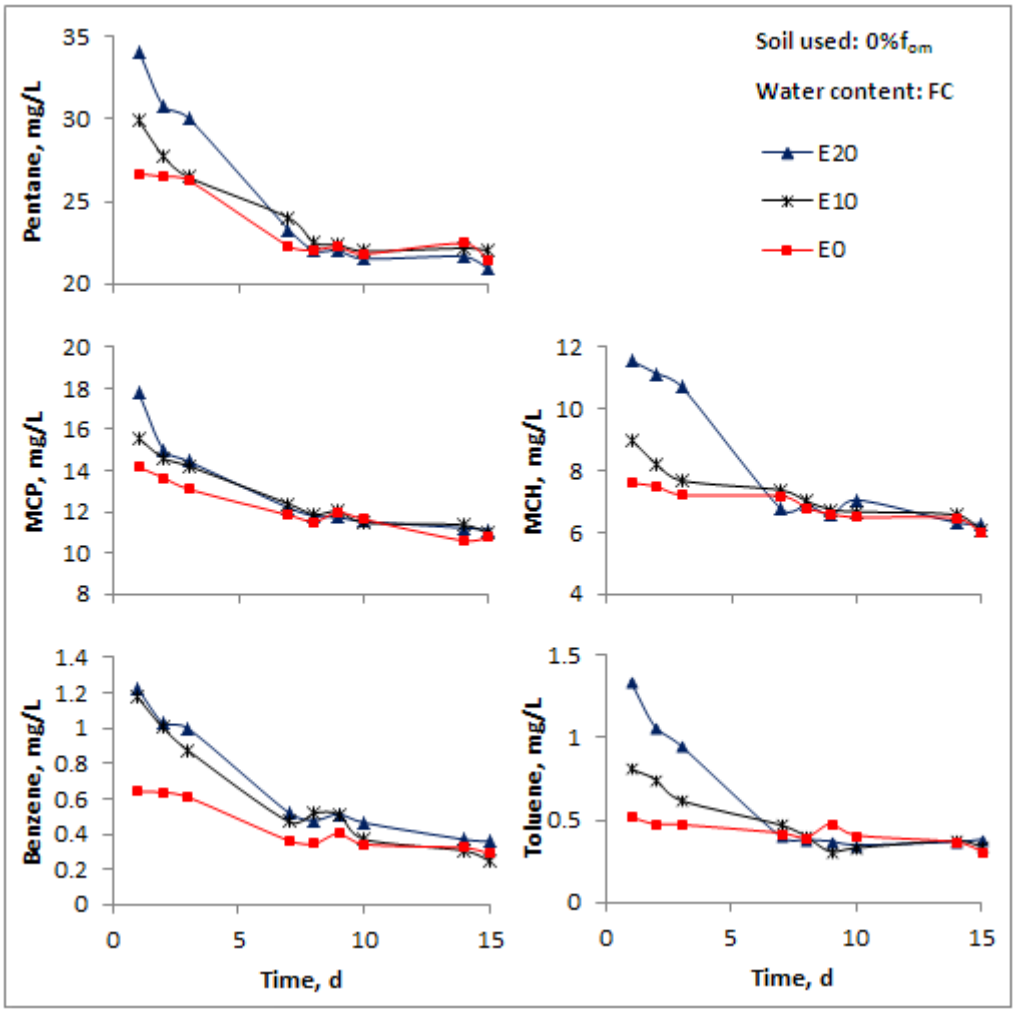

Figure 5.1 Impact of ethanol on the headspace concentrations of gasoline compounds with time for 0%f_{om}.

5.2.1.2 Soil-water interaction of gasoline compounds

The sorption coefficient (K_d), as discussed in Section 2.4.2.1, of gasoline compounds for 0%f_{om} at FC as a function of gasoline composition is shown in Figure 5.2. The values of K_d were calculated using Equation [2.15]. K_d was calculated on a daily basis and the average K_d used as the representative K_d. The standard deviation of all the K_d was calculated and used as the error bar. The presence of ethanol caused a reduction in the K_d of all gasoline compounds. This impact was greatest for benzene with a K_d reduction of 63% compared to the other gasoline compounds between 54

to 62%. Since K_d is the ratio of the concentration of compounds adsorbed by the soil solids to the concentration dissolved in the soil water (Section 2.4.2.1), the reduction in K_d of the ethanol-blended gasoline compounds implies a decrease in adsorption on the soil solids or an increase in partitioning to the soil water. Therefore, the high K_d decrease observed for benzene means lower adsorption or higher partitioning to the soil water. This indicates that the presence of ethanol could have a greater impact on the aromatics than on the alkanes and cycloalkanes in terms of migration to groundwater. Overall, the data show that the addition of ethanol to gasoline at concentrations equal to 10% by volume and higher could reduce the adsorption of gasoline compounds. This reduction in adsorption indicates greater downward migration of gasoline compounds to groundwater after spills. This result contradicts earlier literature observations suggesting that the effect of ethanol on gasoline compounds would be significant for ethanol concentrations higher than 10% (Section 2.3.3), but support the findings of other studies as presented in Section 1.1.

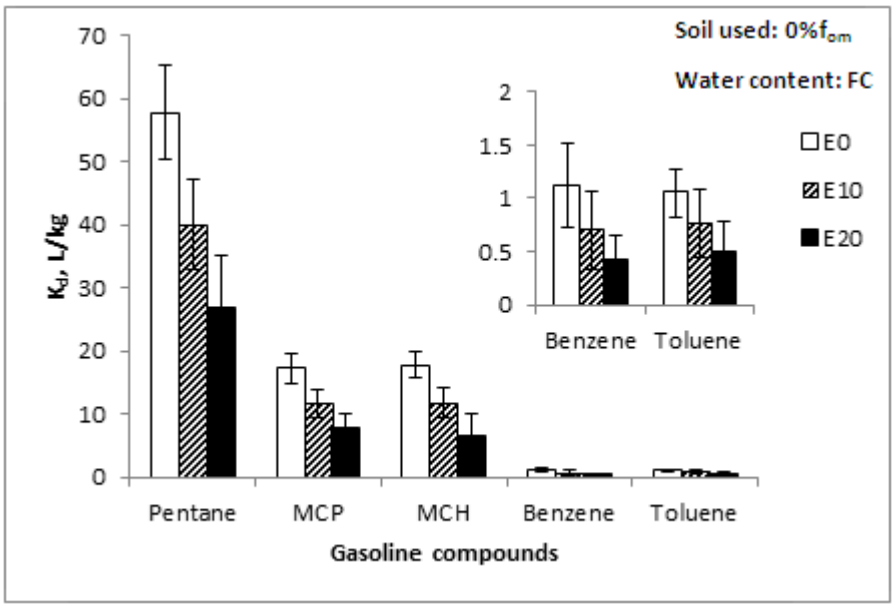

Figure 5.2 Impact of ethanol on the average sorption coefficient (K_d) of gasoline compounds for 0%f_{om} at field capacity.

5.2.1.3 Mass distribution of gasoline compounds between vadose zone phases

Table 5.1 lists the mass percentages of E0 - E20 gasoline compounds in the soil air, soil water and soil solids for 0%f_{om} at field capacity using the microcosm setup. The masses were estimated by fitting measured data into Equations [2.8], [2.9] and [2.11], respectively. The estimated mass percentages were in good agreement with literature values where Dakhel et al. (2003) reported a value of 11.1% for ethanol-blended benzene in the soil air which agrees well with the 6.1 to 11.2% estimated for ethanol-blended benzene in the soil air at equilibrium by this study. More so, similar trend of the mass percentages of the different hydrocarbon groups in the soil water has also been reported by Christophersen et al. (2005). The presence of ethanol caused a drastic reduction in the mass percentages of all gasoline compounds on the soil solids, but raised mass percentages in soil water and soil air. This effect was greatest 4 h after contamination on Day 1, and reduced with time. This again indicates that the impact of ethanol on the sorption and distribution of gasoline compounds would be greatest on the first day of a spill. The reduction in the mass percentages of E10 and E20 gasoline compounds on the soil solids indicates an increase in the mass percentages of gasoline compounds available for transport to the saturated zone. This reduction increased with increasing ethanol volume and was highest for toluene with 62% compared to the other gasoline compounds between 32 to 48%. This supports the earlier observation in Sections 5.2.1.1 and 5.2.1.2 that the increase in groundwater contamination with ethanol-blended gasoline compounds would be greater for the aromatic compounds.

Table 5.1 Impact of 10 and 20% ethanol by volume on the mass distribution of gasoline compounds in 0%f_{om} vadose zone phases.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	E0	**E10**	**E20**	**E0**	**E10**	**E20**	**E0**	**E10**	**E20**	**E0**	**E10**	**E20**	**E0**	**E10**	**E20**
Mass in soil water, %															
1	0.1	0.2	0.3	0.4	0.6	0.8	0.4	0.6	0.9	10.8	24.5	32.2	8.8	17.0	34.8
8	0.1	0.1	0.2	0.4	0.5	0.6	0.3	0.4	0.5	6.8	10.9	12.6	8.1	8.4	9.9
15	0.1	0.1	0.2	0.3	0.4	0.5	0.3	0.4	0.5	4.9	5.1	9.5	5.2	7.1	9.9
Mass in soil air, %															
1	33.6	46.7	66.2	33.5	45.7	64.6	35.1	51.4	82.4	12.8	29.0	38.0	12.2	23.5	48.2
8	28.1	35.2	42.8	28.4	34.9	43.0	30.5	40.1	49.3	8.1	12.8	14.8	11.2	11.7	13.7
15	27.0	34.4	40.6	25.5	32.2	40.5	27.6	34.6	44.8	5.7	6.1	11.2	7.2	9.9	13.7
Mass in soil solids, %															
1	66.3	53.2	33.6	66.1	53.7	34.5	64.5	48.0	16.7	76.4	46.5	29.8	79.1	59.5	17.1
8	71.7	64.4	56.7	71.1	64.4	56.0	69.0	59.1	49.7	85.0	76.2	72.4	80.7	79.8	76.2
15	72.5	65.0	58.6	73.9	67.0	58.3	71.7	64.5	54.0	89.3	88.6	79.1	87.5	82.8	76.2

All experiments were conducted using 0%f_{om} at FC

5.2.2 Impact of SOM on the sorption and phase distribution of E20 gasoline compounds

5.2.2.1 Sorption of E20 gasoline compounds

Figure 5.3 shows the concentrations of E20 gasoline compounds in the headspace of microcosms with time as a function of SOM fraction of soils. All E20 gasoline compounds persisted at detectable concentrations at the headspace throughout the 15 days duration of the experiment except for ethanol that decreased continuously with time and completely disappeared from the headspace on Day 13. The decrease in the headspace concentration of all E20 gasoline compounds describes the physical sorption to the soil since biodegradation is not expected to occur due to the sterilisation of the soils (Section 3.3.1). Generally, two phases of sorption were observed. A rapid sorption during the first three days after contamination followed by a slower sorption from Day 6 onwards until equilibrium was reached. The two phases of sorption observed in the present study is a common observation in sorption studies (Allen-King et al., 1994; Gaston and Locke, 1995; Höhener et al., 2003). The slower sorption has been interpreted as intraparticle diffusion-limited approach of equilibrium between soil phases (Höhener et al., 2003; Site, 2001).

Previous studies have shown that SOM could increase the sorption of single hydrophobic compounds (Chen et al., 2007; Li et al., 2009). This study has found the same to be true for a complex mixture like ethanol-blended gasoline. The increase in the SOM fraction of soils resulted in rapid and greater sorption of all E20 gasoline compounds except for ethanol that had similar sorption for all SOM fractions. Ethanol has low octanol-water partition coefficient (K_{ow}) of 0.5 compared to the gasoline compounds that

have K_{ow} ranging from 134.9 to 7585.8 (Yaws, 2008). Hence, ethanol partitioned readily to soil water and was not affected by SOM. The observed behaviour of ethanol is consistent with previous findings for highly polar compounds. For example, Guo et al. (2010) found that SOM would have a higher sorption capacity for a contaminant with a lower solubility or a higher K_{ow} value. However, for a contaminant with a higher solubility or a lower K_{ow} value, Shi et al. (2010) noted that the sorption would be largely influenced by the presence of clay minerals rather than SOM. Since SOM has high specific surface area and porosity that can promote sorption (Allen-King et al., 2002), the increasing sorption of all gasoline compounds by soil with increasing SOM fraction could be due to the increase in the surface area and porosity of the soils as presented in Table 4.4 in Section 4.3. Although the impact of SOM on the sorption of gasoline compounds varied with time and compounds, it was generally greatest on Day 1 and affected the aromatics to a greater extent of 76 to 89% than the alkanes and cycloalkanes of 29 to 59%. The difference in impact amongst the hydrocarbon groups could be due to the difference in bond lengths, where the C-C bond length of the aromatics is $1.39*10^{-10}$ m compared to that of the alkanes and cycloalkanes of $1.54*10^{-10}$ m (Solomons and Fryhle, 2011). Thus, aromatics are expected to have a higher initial sorption with increasing porosity in the soil. Overall, the data indicate that SOM promoted the sorption of all gasoline compounds, but had no significant impact on the sorption of ethanol. Among the gasoline compounds, the aromatics were promoted to a greater extent than the alkanes and cycloalkanes.

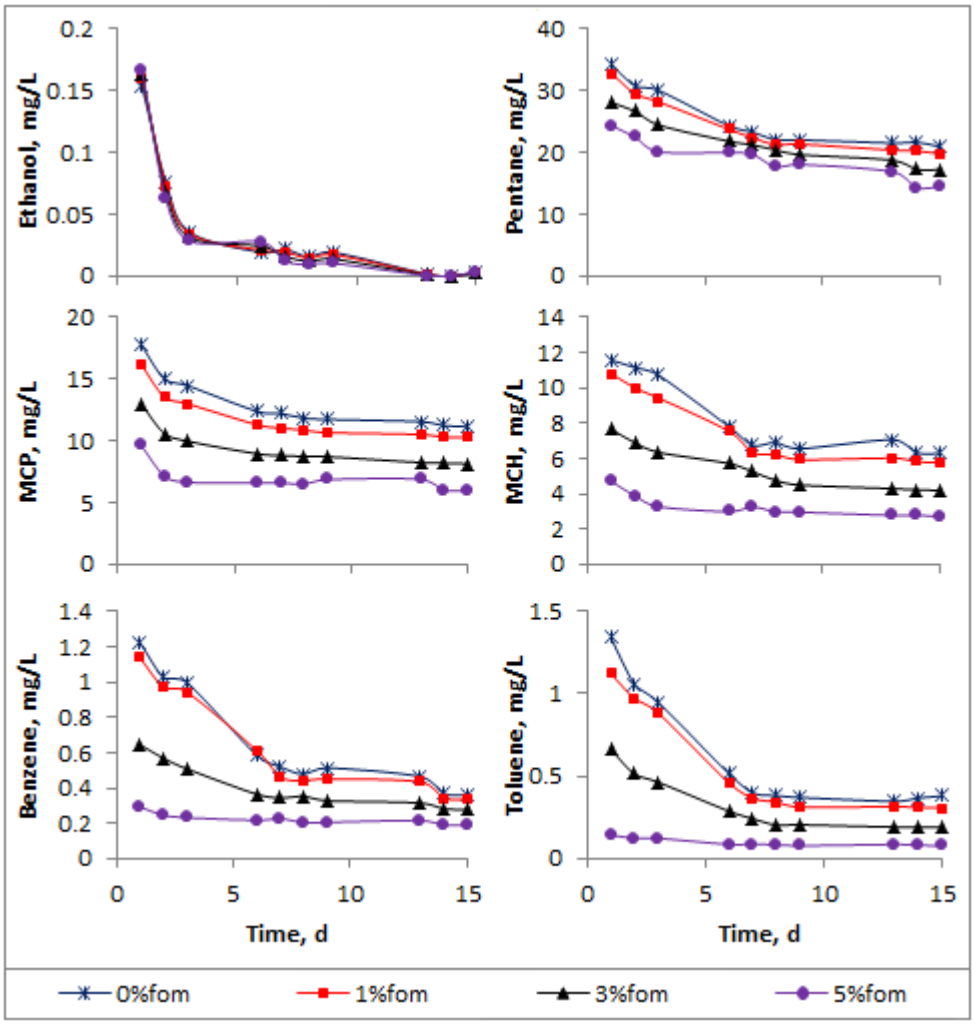

Figure 5.3 Headspace concentrations of E20 gasoline compounds with time as a function of SOM fraction of soils.

5.2.2.2 Soil-water interaction of E20 gasoline compounds

The effect of SOM fraction (f_{om}) of soils on the soil-water interaction of E20 gasoline compounds in the vadose zone is illustrated with the average sorption coefficient (K_d) of E20 gasoline compounds in soils with varying f_{om} in Figure 5.4. The K_d values were estimated as described in Section 3.3.5 using Equation [2.15]. The K_d of all gasoline compounds increased with increasing f_{om}, suggesting an increase in the adsorption of gasoline compounds on the soil solids or a reduction in the concentrations of gasoline compounds in the soil water. This impact was greatest for the

aromatics, with K_d increased by a maximum of 7 times, compared with the cycloalkanes (4 times) and the alkanes (2 times), for 0 to 5% increase in f_{om}. As reported by Site (2001), the K_d values for benzene, toluene and xylenes were increased with increasing surface area (SA) of adsorbents. The K_d value of pyrene was also found to increase with increasing SA of the adsorbents (Wang et al., 2008b). Therefore, one explanation for the observed increase in K_d with increasing f_{om} of soils could be the increase in the surface area of soils as listed in Table 4.4 in Section 4.3. Another explanation could be the reduction in available soil water in the soil with increasing f_{om} due to the high water absorption capacity of SOM (Page, 1982).

Despite the difference in contaminant mixtures, the K_d values obtained for 0%f_{om} in this study, 0.4 L/kg for benzene and 0.5 L/kg for toluene, were comparable to those reported for sand in the literature. For example Joo et al. (2008) reported K_d values of 0.2 L/kg for benzene and 0.3 L/kg for toluene, and Christophersen et al. (2005) reported K_d values of 0.02 L/kg for benzene and 0.04 L/kg for toluene. The slight differences between the K_d values can be attributed to the slight differences in the soil and contaminant mixture used (Allen-King et al., 2002). Similar observations on the direct relationship between K_d and SOM have been reported for a wide range of organic contaminants and adsorbents (Celis et al., 2006; Chen et al., 2007; Chiou, 2002; Li et al., 2009; Shi et al., 2010). Therefore, the data indicate that SOM increased the adsorption of E20 gasoline compounds on the soil solids but reduced their partitioning to the soil water. This effect was greater for the aromatics compared to the cycloalkanes and alkanes.

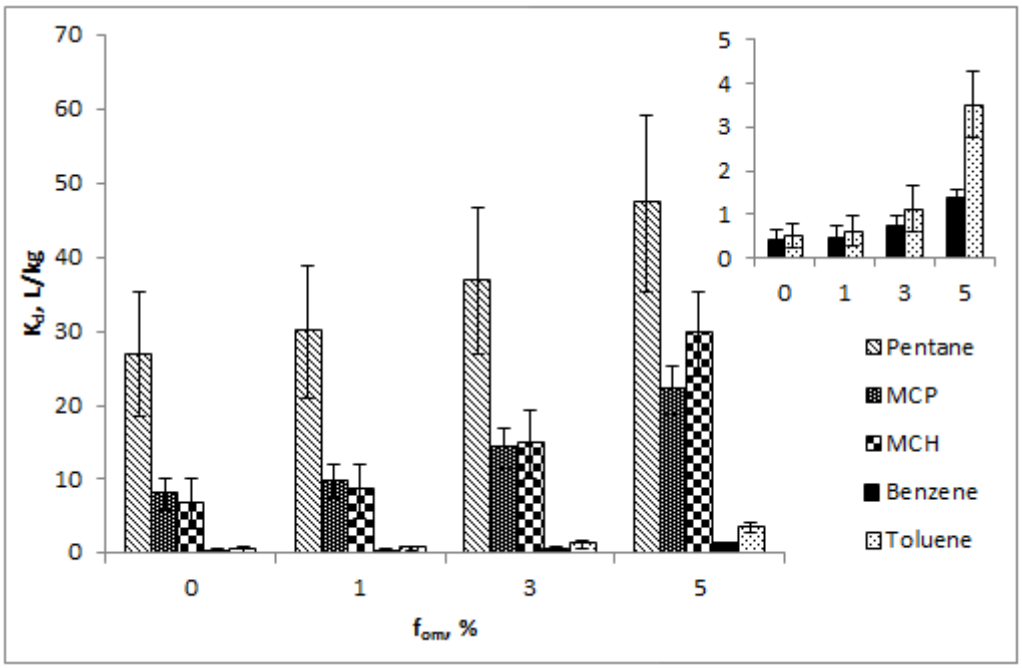

Figure 5.4 Average sorption coefficient (K_d) of E20 gasoline compounds as a function of SOM fraction of soils.

5.2.2.3 Retardation of the migration of E20 gasoline compounds

Figure 5.5 shows the increase in the retardation factor (R) values for E20 gasoline compounds with increasing SOM fraction (f_{om}) of the soils. R was estimated from K_d values using Equation [2.16] as described in Section 3.3.5, and represents the degree of retardation of the migration of the gasoline compounds due to sorption as mentioned in Section 2.4.2.2. Figure 5.5 shows that SOM promoted the R of all E20 gasoline compounds, implying a reduction in the migration of E20 gasoline compounds in the vadose zone. This effect increased with decreasing solubility of gasoline compounds hence was greatest for the cycloalkanes (0 – 46.8) compared to the alkanes (0 – 25.7) and the aromatics (0 – 6.5). The R of gasoline compounds with similar solubility, such as pentane and MCP of 0.04 g/L (Yaws, 2008), were similarly impacted. The difference in the R values for

gasoline compounds could result in different distributions for the gasoline compounds in the soil (Johnson and Perrott, 1991).

By substituting Joo et al. (2008) K_d values of 0.2 L/kg for benzene and 0.3 L/kg for toluene into Equation [2.16] for 0%f_{om}, which is similar in SOM fraction to the aquifer sand used by Joo and co-workers, R values of 1.61 for benzene and 1.91 for toluene were obtained. These values, though obtained from a contaminant mixture comprising only aromatics, were found similar to the R values of 2.29 for benzene and 2.53 for toluene obtained in this study which used a contaminant mixture consisting of alkanes, cycloalkanes, aromatics and alcohol. Also, the benzene and toluene R values obtained from the 0%f_{om} soil were in good agreement with the R values of 1.24 for benzene and 1.93 for toluene in sand reported by Höhener et al. (2006). However, this study R values were found to be entirely different from those reported for clay, 117.2 for benzene and 734 for toluene (Myrand et al., 1992), and for fine silty loam, 193.0 for benzene and 218.0 for toluene (Johnson and Perrott, 1991). The vast difference between the R values from different soils, as compared with the R values from different contaminant mixture, suggests that R of gasoline compounds could be highly site specific and that the properties of soils is likely to have a greater influence on the R of gasoline compounds than the composition of gasoline.

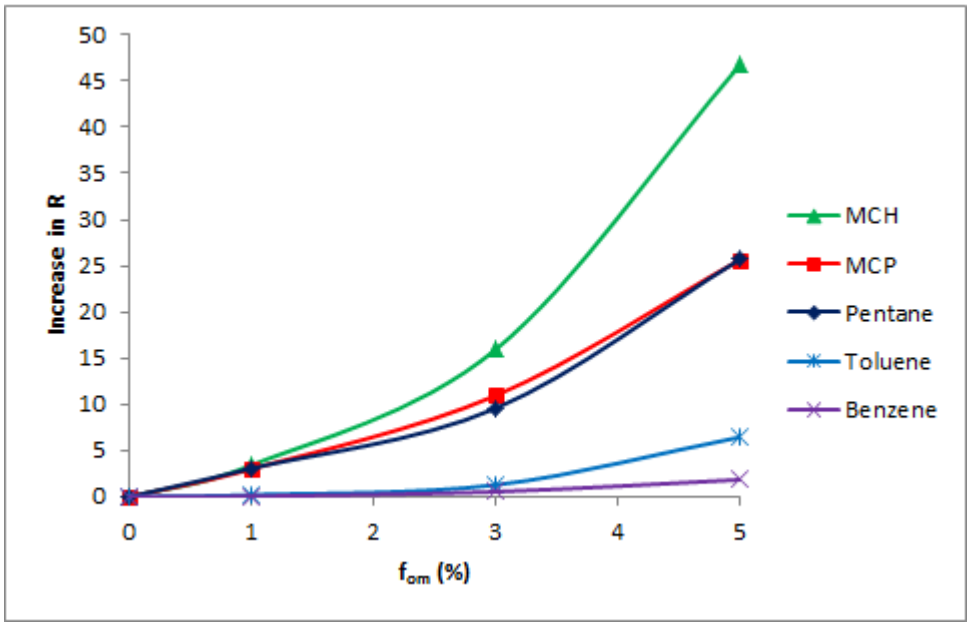

Figure 5.5 Retardation factors (R) of E20 gasoline compounds as a function of SOM fraction of soils.

5.2.2.4 Mass distribution of E20 gasoline compounds between vadose zone phases

The mass distribution of E20 gasoline compounds to the soil air, soil water and soil solid phases as a function of SOM fraction (f_{om}) of soils is presented in Table 5.2. The masses were similarly estimated as described earlier in Section 5.2.1.3. The mass distribution of gasoline compounds to the vadose zone phases changed with time. While the mass of gasoline compounds on the soil solids increased with time, the mass in the soil air and soil water decreased with time for all soils tested. The increase in f_{om} of soils increased mass distribution to the soil solids and caused a rapid uptake of all gasoline compounds 4 h after contamination on Day 1. This effect was greatest for the aromatics, with a maximum increase in adsorption on the soil solids of 75% when comparing the 0 and 5%f_{om} soils, compared to the cycloalkanes of 54% and the alkanes of 26%. Water solubility seemed to be an important property determining the impact of

SOM on the adsorption of gasoline compounds on the soil solids. The mass distribution in 0%f_{om} on Day 1 shows that the aromatics had the highest mass in the soil water compared to the cycloalkanes and the alkanes. It is then likely that the addition of SOM to soils affected the available water in the experimental system more than it affected the available air due to the high water absorption capability of SOM (Page, 1982). Consequently, most of the dissolved masses were adsorbed on the soil solids. The adsorption of some of the masses in the soil air may have been prompted by the increase in the surface area of soils with increasing f_{om} as presented in Table 4.4 in Section 4.3 (Site, 2001; Wang et al., 2008b). In contrast to impact on Day 1, SOM impacted a general lower mass distribution to the soil solids for all gasoline compounds on Day 15, suggesting that the influence of SOM on sorption is likely to be predominant on Day 1 of a spill. More so, the mass distribution to the soil solids of the cycloalkanes was impacted to a greater extent of 23 to 29% than those of the alkanes and aromatics of only 11 to 19%, suggesting that the degree of impact of SOM on the mass distribution of gasoline compounds could vary with time.

In summary, the data show that SOM could enhance the mass distribution of E20 gasoline compounds to the soil solids in the vadose zone. The degree of the impact is likely to vary with time among the gasoline compounds. The less hydrophobic compounds, such as the aromatics, are more likely to be impacted to a greater extent before equilibrium, while the more hydrophobic compounds, such as the cycloalkanes, could be impacted to a larger extent at equilibrium. Hence, this result offers an understanding into the mass distribution of E20 gasoline compounds to the vadose zone phases following a spill on soils with varying SOM contents.

Table 5.2 Mass distribution of E20 gasoline compounds in the vadose zone as a function of SOM fraction of soils.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %
							0%f_{om}								
1	66.2	33.6	0.3	64.6	34.5	0.8	82.4	16.7	0.9	38.0	29.8	32.2	48.2	17.1	34.8
8	42.8	56.7	0.2	43.0	56.0	0.6	49.3	49.7	0.5	14.9	72.4	12.6	13.7	76.2	9.9
15	40.6	58.6	0.2	40.5	58.3	0.5	44.8	54.0	0.5	11.2	79.1	9.5	13.7	76.1	9.9
							1%f_{om}								
1	61.5	38.3	0.2	56.9	42.3	0.8	74.4	24.8	0.8	34.2	35.9	29.9	39.0	31.9	29.1
8	39.9	59.5	0.2	38.3	60.8	0.5	42.9	56.1	0.5	13.3	74.8	11.7	11.9	79.0	8.9
15	37.2	62.0	0.1	36.2	62.7	0.5	39.8	59.1	0.5	10.1	80.8	8.8	10.7	81.0	8.0
							3%f_{om}								
1	50.4	49.4	0.2	43.8	55.6	0.6	50.4	49.0	0.6	18.6	64.5	17.0	22.1	60.7	17.2
8	36.7	62.8	0.2	29.5	69.8	0.4	31.4	67.9	0.4	10.2	80.4	9.3	6.8	87.8	5.3
15	31.0	68.3	0.1	27.5	71.8	0.4	27.7	71.5	0.3	8.0	84.4	7.3	6.4	88.4	5.0
							5%f_{om}								
1	40.4	59.5	0.2	30.0	69.6	0.5	28.6	71.0	0.4	7.8	84.5	7.7	4.4	91.8	3.7
8	29.3	70.3	0.1	20.3	79.2	0.3	18.2	81.4	0.2	5.4	89.1	5.4	2.6	95.1	2.2
15	24.0	75.4	0.1	18.6	80.8	0.3	16.5	83.0	0.2	5.1	89.8	5.1	2.4	95.5	2.0

5.2.3 Ethanol-influenced changes on the impact of SOM on the sorption of gasoline compounds

Table 5.3 lists the average sorption coefficient (K_d) values obtained in $0\%f_{om}$ and $5\%f_{om}$ soils for the E0, E10 and E20 gasoline compounds. The presence of ethanol caused a significant reduction in the K_d of all gasoline compounds in both $0\%f_{om}$ and $5\%f_{om}$, showing a reduction in the amount of gasoline compounds adsorbed on the soil solids with increasing SOM. This reduction increased with increasing volume of ethanol. Ethanol also reduced the SOM-induced increase in K_d for all gasoline compounds, implying a reduction in the SOM sorptive capability for gasoline compounds. This impact on the sorptive capability of SOM could be due to changes in conformation of the SOM matrix induced by changes in the gasoline polarity resulting from the presence of ethanol (Brusseau et al., 1991; Ju and Young, 2005). Previous studies have shown that low polarity of SOM could lead to high sorption of contaminant and vice versa (Chefetz et al., 2000; Guo et al., 2010; Shi et al., 2010). Therefore, it is likely that the presence of ethanol increased the polarity of the SOM which resulted in the reduction of K_d. The change in gasoline polarity with the addition of 10 and 20% ethanol by volume was expected since ethanol impact on gasoline has been reported to be significant for concentrations of 10% and above (Section 1.1). Among the gasoline compounds, the cycloalkanes were impacted to a greater extent, with a maximum decrease in the SOM-induced increase in K_d of 46 and 76%, than the aromatics of 43 and 73% and the alkanes of 36 and 60% for 10 and 20% ethanol, respectively. This reduction in the SOM sorptive capability signifies reduction in the amount of gasoline compounds retained by the soil solids in the vadose zone. It also denotes increase in the amount of gasoline compounds in the mobile

phases (soil air and soil water) which in turn represents increase in groundwater contamination potential (Yu, 1995).

Table 5.3 Impact of ethanol on average K_d increase by SOM.

Gasoline blend	**Compound**	**K_d, L/kg**		**Increase in K_d**	
		0%f_{om}	**5%f_{om}**	**L/kg**	**%**
E0	Pentane	57.8	108.7	50.9	88
	MCP	17.3	57.9	40.6	235
	MCH	17.8	111.5	93.7	526
	Benzene	1.1	3.4	2.3	209
	Toluene	1.1	12.1	11.0	1000
E10	Pentane	40.1	72.9	32.8	82
	MCP	11.8	35.9	24.1	204
	MCH	11.8	62.8	51.0	432
	Benzene	0.7	2.3	1.6	229
	Toluene	0.8	7.1	6.3	788
E20	Pentane	26.9	47.3	20.4	76
	MCP	8.0	22.0	14.0	175
	MCH	6.7	29.6	22.9	342
	Benzene	0.4	1.4	1.0	250
	Toluene	0.5	3.5	3.0	600

5.2.4 Impact of soil water content on SOM sorptive capability for E20 gasoline compounds

5.2.4.1 Sorption of E20 gasoline compounds

The impact of soil water content on the sorptive capability of SOM for E20 gasoline compounds was investigated by comparing the sorption of E20 gasoline compounds by 5%f_{om} wetted to 0, 4.5 and 9% water contents by weight as used in Section 4.5. The sorption of the E20 gasoline compounds at the various water contents was monitored by measuring the decrease in

the headspace vapour concentrations as described in Section 3.3.3. The difference in the headspace vapour concentrations of the E20 gasoline compounds for the three water contents is presented in Figure 5.6. The increase in the water content of 5%f_{om} resulted in increase in the headspace concentrations of all E20 gasoline compounds. This indicates decrease in the sorption of all gasoline compounds by the soil. As discussed in Section 2.2.3.6, this decrease in sorption could be due to the filling of the SOM pores with soil water and thus the blockage of the high-energy sorption sites resulting in a substantial reduction in the surface activities of the SOM (Steinberg and Kreamer, 1993) and slow vapour phase transport (Johnson and Perrott, 1991).

At 0% water content, all aromatics were completely sorbed by the soil three days after contamination while the alkanes and cycloalkanes persisted at negligible concentrations at the headspace of the microcosm throughout the 15 days duration of the experiment. The percentages of the alkanes and cycloalkanes sorbed on Day 15 were 99.5% for the alkanes and 99.8 to 99.9% for the cycloalkanes. At 4.5% and 9% water contents, complete sorption was not observed for any gasoline compounds throughout the experimental period. The percentages of sorption on Day 15 for 4.5% were 92.8% for alkanes, 97.4 to 98.4% for the cycloalkanes and 98.9 to 99.5% for the aromatics. In contrast, the percentages of sorption on Day 15 for 9% were 90.3% for the alkanes, 92.6 to 93.4% for the cycloalkanes and 98.0 to 99.0% for the aromatics. This result clearly shows that the sorptive capability of SOM in soil could be reduced with increasing soil water content, suggesting that the degree of E20 gasoline compounds retention in the vadose zone by soil could differ during the dry summer and wet winter.

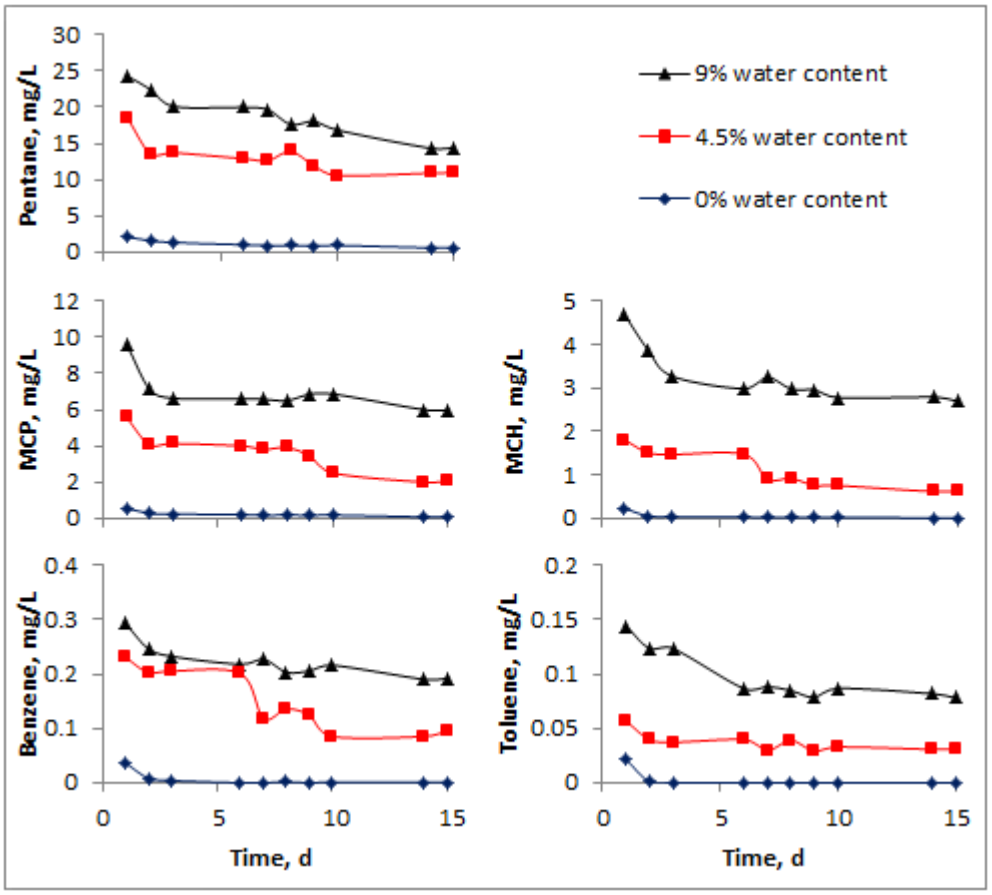

Figure 5.6 Headspace vapour concentrations of E20 gasoline compounds with time as a function of soil water content of 5%f_{om}.

5.2.4.2 Soil-water interaction of E20 gasoline compounds

Figure 5.7 shows the changes in the average K_d values for E20 gasoline compounds with changing soil water content of 5%f_{om}. The K_d values for all gasoline compounds decreased with increasing soil water content, implying decrease in adsorption on the soil solids or increase in concentrations in the soil water. As reported by Site (2001), the increase in the surface area (SA) of soils increased the K_d of gasoline compounds. Therefore, the observed decrease in the K_d of E20 gasoline compounds with increasing soil water content could be due to the reduction in the SA of the soil. According to Steinberg and Kreamer (1993), this reduction in the SA of soil could be due to the blockage of some of its sorption sites by the additional soil

water. As expected, the decrease in K_d was greatest on the most soluble gasoline compound (benzene). The increase in soil water content promoted compound-water contact and therefore enhanced the partitioning of compounds to the water phase. Thus, as observed for inorganic soils and other organic compounds (Acher et al., 1989; Johnson and Perrott, 1991; Ong and Lion, 1991; Site, 2001; Smith et al., 1990; Steinberg and Kreamer, 1993), the increase in SOM water content could decrease its sorptive capability for ethanol-blended gasoline compounds.

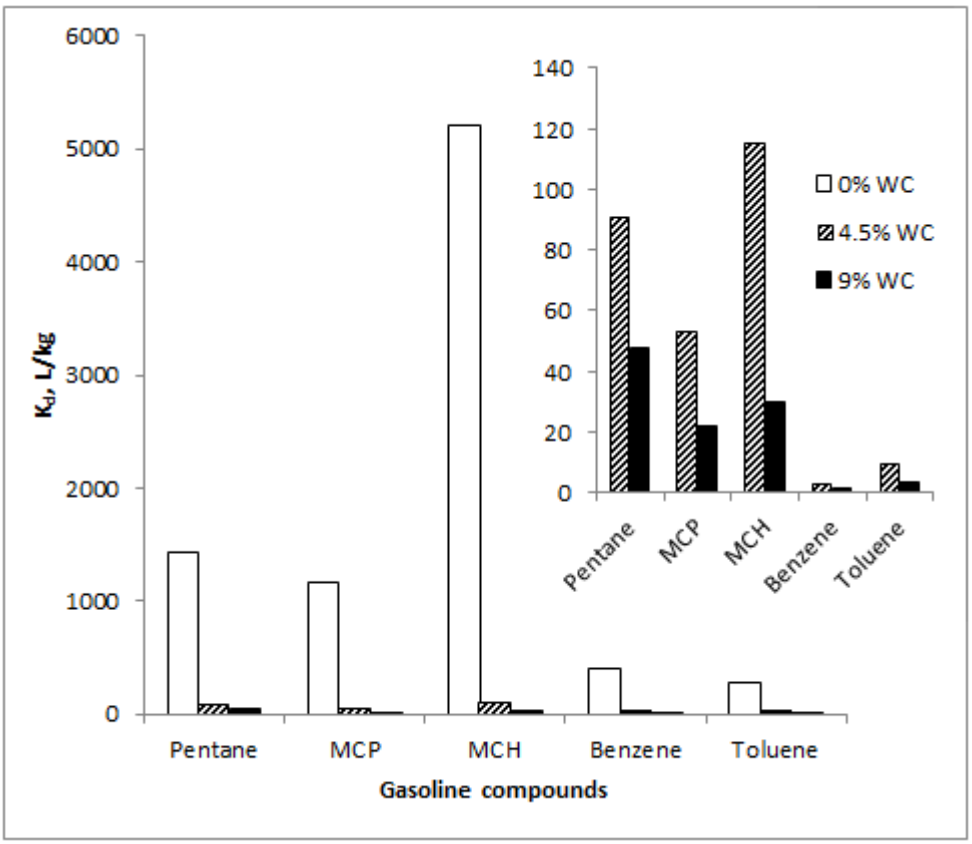

Figure 5.7 Changes in the average sorption coefficient (K_d) of E20 gasoline compounds with increasing soil water content of 5%f_{om}.

5.2.4.3 Mass distribution of E20 gasoline compounds between vadose zone phases

Tables 5.4 and 5.5 compares the changes in the mass percentages of E20 and E0 gasoline compounds, respectively, in the soil water, soil air and soil solid phases with increasing soil water content. The increase in soil water content caused an increase in the partitioning of all E20 gasoline compounds to the soil water and soil air, but resulted in a decrease in adsorption on the soil solids. As expected, the increase in the partitioning of compounds to the soil water was greatest for the most soluble gasoline compound, benzene, while the increase in the partitioning of compounds to the soil air was greatest for the most volatile gasoline compound, pentane. The decrease in the adsorption of compounds on the soil solids was lowest for the aromatics, probably due to their lower hydrophobicity. As the water content of the soil increases, the soil solid surfaces are gradually blocked with water thereby restricting the more hydrophobic gasoline compounds, such as the cycloalkanes and alkanes, to the headspace to a greater extent compared with the less hydrophobic gasoline compounds, such as the aromatics. This lower restriction of the aromatics to the headspace may have aided their lower reduction in adsorption. Generally, the data show that an increase in soil water content could reduce the sorptive capability of SOM in soils and, therefore, is likely to reduce the mass distribution of gasoline compounds to the soil solids. With reference to the mass distribution of E0 gasoline compounds as listed in Table 5.5, the data of Table 5.4 is of great significance as it provides an insight into how ethanol-blended gasoline compounds could be distributed between the different phases of high SOM content soils during the dry and wet seasons.

Table 5.4 Mass distribution of E20 gasoline compounds between different vadose zone phases as a function of soil water content of 5%f_{om}.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%
Mass in soil water, %															
1	0	0.1	0.2	0	0.1	0.5	0	0.1	0.4	0	3.0	7.7	0	0.7	3.7
8	0	0	0.1	0	0.1	0.3	0	0	0.2	0	1.8	5.4	0	0.5	2.2
15	0	0	0.1	0	0.1	0.3	0	0	0.2	0	1.3	5.1	0	0.4	2.0
Mass in soil air, %															
1	3.2	26.9	40.4	1.9	18.1	30.0	1.6	11.6	28.6	1.1	6.4	7.8	0.7	1.8	4.4
8	1.3	18.8	29.3	0.6	12.8	20.3	0.1	5.9	18.2	0	3.8	5.4	0	1.3	2.6
15	1.1	17.3	24.0	0.3	6.7	18.6	0.1	4.1	16.5	0	2.7	5.1	0	1.0	2.4
Mass in soil solids, %															
1	96.8	73.0	59.5	98.1	81.7	69.6	98.4	88.4	71.0	98.8	90.6	84.5	99.3	97.4	91.8
8	98.6	81.0	70.3	99.3	87.0	79.2	99.8	94.0	81.4	99.9	94.3	89.1	99.9	98.1	95.1
15	98.8	82.4	75.4	99.6	93.0	80.8	99.8	95.8	83.0	99.9	96.0	89.8	99.9	98.5	95.5

0%, 4.5% and 9% are gravimetric water contents of 5%f_{om}

Table 5.5 Mass distribution of E0 gasoline compounds between different vadose zone phases as a function of soil water content of 5%f_{om}.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%
Mass in soil water, %															
1	0	0	0.1	0	0.1	0.2	0	0	0.1	0	1.4	3.3	0	0.4	1.2
8	0	0	0.1	0	0	0.1	0	0	0.1	0	0.9	2.6	0	0.2	0.7
15	0	0	0.1	0	0	0.1	0	0	0.1	0	0.8	2.1	0	0.2	0.6
Mass in soil air, %															
1	2.4	16.5	19.2	0.8	10.0	11.5	1.5	6.7	8.0	0.4	2.9	3.3	0.4	1.0	1.4
8	0.5	12.0	16.3	0.3	5.9	9.2	0.6	3.9	5.8	0	1.8	2.7	0.1	0.6	0.8
15	0.3	9.7	13.7	0.2	5.3	7.9	0.4	3.4	5.0	0	1.7	2.1	0.1	0.6	0.7
Mass in soil solids, %															
1	97.6	83.5	80.7	99.2	90.0	88.3	98.5	93.2	91.9	96.6	95.8	93.4	99.6	98.6	97.4
8	99.4	87.9	83.5	99.6	93.9	90.5	99.3	95.9	94.0	99.9	97.2	94.6	99.8	99.1	98.4
15	99.6	90.1	86.1	99.7	94.5	91.9	99.5	96.5	94.9	99.9	97.4	95.8	99.8	99.1	98.6

5.3 Mini-lysimeter experiment

5.3.1 Impact of ethanol on the vapour phase transport of gasoline compounds in the vadose zone

Figure 5.8 shows the depth profiles of the vapour phase concentrations of pentane, MCP and benzene on Days 1, 3, 5, 8, 10, 12 and 15 after contamination as a function of gasoline composition in the mini-lysimeter (Section 3.4.3). The three gasoline compounds were chosen because they are good representatives of the three hydrocarbon groups that constituted the synthetic gasoline mixture (Section 3.1). The concentration profiles were shown for the selected sampling days to make the transport trend of each compound more visible. All experiments were conducted with 0%f_{om} to eliminate interference with SOM. The vapour phase concentrations of all gasoline compounds generally decreased with time due to adsorption on the soil solids and partitioning to the soil water. The addition of ethanol to gasoline had varied effects on the vapour phase concentrations of the gasoline compounds in the vadose zone (0 - 28 cm). It promoted the vapour phase concentrations of pentane (the alkanes representative) and benzene (the aromatics representative) in the first five days after contamination, but reduced the vapour phase concentration of MCP (the cycloalkanes representative) throughout the duration of the experiment. The differences in property of the gasoline compounds as listed in Table 3.1 in Section 3.1 and as discussed in Section 2.2.4 could be the reason for the different impacts. The decrease in the vapour phase concentration of the gasoline compounds could be due to partitioning to the soil water as a result of cosolvent effect.

A careful comparison of the vapour phase concentrations of the E0, E10 and E20 gasoline compounds in the vadose zone revealed that the decrease in the vapour concentrations of the E10 and E20 cycloalkanes increased with depth. Since the volumetric water content of the vadose zone increased with increasing depth (see Figure 4.3 in Section 4.4.1), the higher decrease in the vapour phase concentration of the E10 and E20 cycloalkanes with increasing depth suggests that the cosolvent effect of ethanol on the cycloalkanes increased with increasing availability of soil water. Also, the promotion of the vapour phase concentrations of the E10 and E20 alkanes and aromatics was found to decrease with increasing depth in the vadose zone, indicating the dominance of the cosolvent effect of ethanol with increasing soil water. Therefore, the negligible vapour phase concentrations of the E10 and E20 gasoline compounds measured at the groundwater zone could be attributed to the dominance of the cosolvent effect of ethanol in that zone. This agrees with the decrease in the K_d of gasoline compounds in the presence of 10 and 20% ethanol observed in the microcosm experiments (Section 5.2.1.2).

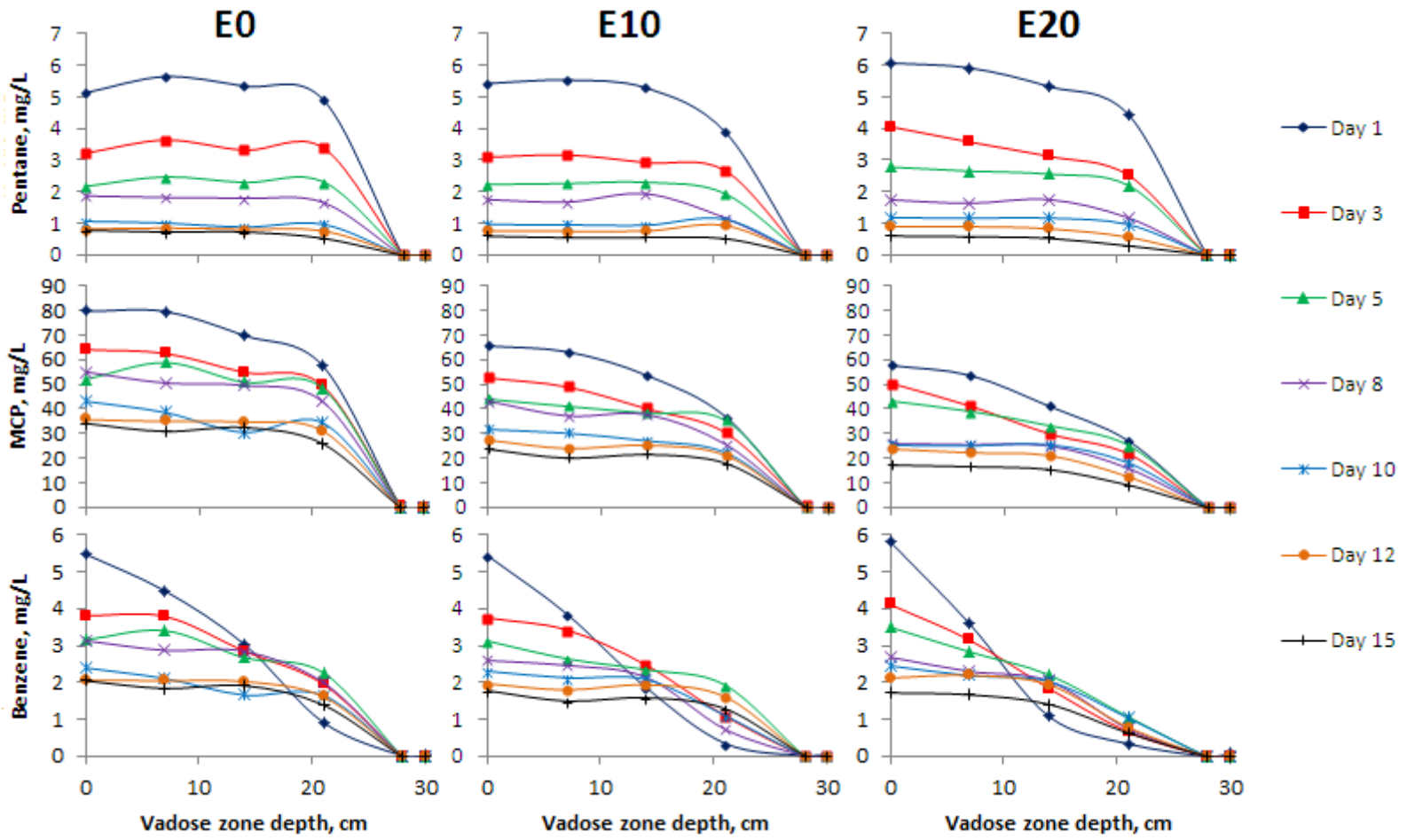

Figure 5.8 Impact of ethanol on the vapour phase transport of gasoline compounds in 0%f_{om} vadose zone.

5.3.2 Impact of SOM on the vapour phase transport of E20 gasoline compounds

The depth profiles of the vapour phase concentrations of the E20 gasoline compounds in vadose zones with varying SOM fractions are shown in Figure 5.9. The concentration profiles are shown for only the representative E20 gasoline compounds in $0\%f_{om}$ and $5\%f_{om}$ on Days 1, 3, 5, 8, 10, 12 and 15 to reduce complexity. The concentration profiles of the representative compounds in $1\%f_{om}$ and $3\%f_{om}$ exhibited behaviours that are amid those of $0\%f_{om}$ and $5\%f_{om}$ (see Appendix C). The concentration profiles of the less volatile gasoline compounds (toluene and MCH) are prone to scatter probably due to suppression by the highly volatile representative compounds (see Appendix D). Evidence of such suppression has been reported for less volatile gasoline compounds, such as octane, 1,2,4-trimethylbenzene and decane (Christophersen et al., 2005; Pasteris et al., 2002). The diffusive transport of all compounds occurred from the source zone (0 cm) to the lower section of the vadose zone. All compounds, except ethanol, were detected at the very low levels at the groundwater zone (28 - 30 cm) throughout the experimental duration for $0\%f_{om}$. As expected for a polar compound, ethanol had a significant vapour concentration at the groundwater zone due to less interaction with the soil solids (Dakhel et al., 2003). This behaviour of ethanol is not supposed to trigger any environmental concern as ethanol is highly degradable and has been reported to be completely attenuated near the source zone in a live soil lysimeter experiment (Dakhel et al., 2003). On the contrary, vapours of all compounds were detected at the groundwater zone of $5\%f_{om}$ 4 h after contamination on Day 1. SOM increased the porosity of the vadose zone from 40% for $0\%f_{om}$ to 47% for $5\%f_{om}$, hence, seemed to have promoted the vapour phase transport of compounds in $5\%f_{om}$ vadose zone. For

ethanol, the lower concentrations measured at the groundwater zone of 5%f_{om} suggests that SOM impacted its partitioning to the soil water to a greater extent than its vapour phase transport to the groundwater zone. Similar high partitioning of ethanol to the water phase in the vadose zone and the accompanying low vapour phase transport to the groundwater has been reported (Dakhel et al., 2003; McDowell and Powers, 2003; Powers and McDowell, 2001). For the gasoline compounds, increasing SOM content promoted their vapour phase transport to the groundwater zone. This effect was more visible on Days 5 to 15 for pentane and MCP, but only visible on Day 8 for benzene. The higher ease of partitioning to the water phase of benzene due to its lower hydrophobicity could be the possible reason for its insignificant change in vapour phase concentrations at the groundwater zone even with a 7% increase in the porosity of the vadose zone. Therefore, this result shows that SOM could reduce the vapour phase transport of the less hydrophobic gasoline compounds to the groundwater by retaining more soil water in the vadose zone for partitioning, but may promote the vapour phase transport of the more hydrophobic gasoline compounds to the groundwater by increasing the porosity of the vadose zone. This supports the enhanced water transport with increasing SOM content at FC observed during the commissioning of the mini-lysimeter (Section 4.4.2).

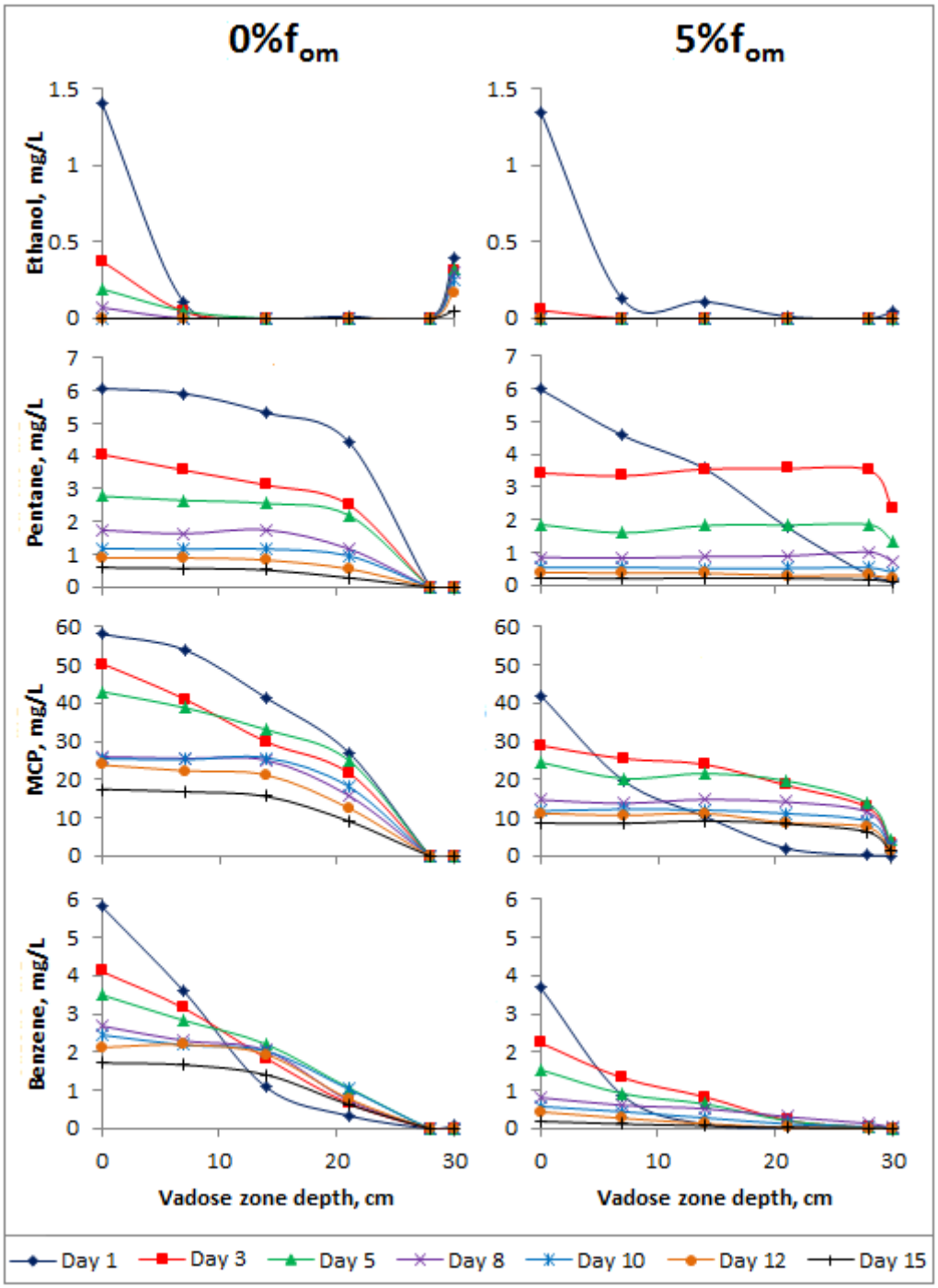

Figure 5.9 Vadose zone depth profiles of vapour phase concentrations of E20 gasoline compounds as a function of SOM fraction of soils.

5.4.3 Ethanol-influenced changes on the impact of SOM on the vapour phase transport of gasoline compounds

Figure 5.10 shows the changes in the impact of SOM on the vapour phase transport of gasoline compounds in the vadose zone due to the presence of ethanol. The vapour phase transport of E0 and E20 gasoline compounds is compared in an SOM-rich soil (5%f_{om}) on selected days across the duration of the experiment. The vapour phase transport of the E0 gasoline compounds are used as the benchmarks. Thus, any deviations in vapour phase transport from the benchmarks by E20 gasoline compounds are interpreted as the impact of ethanol. As can be seen from Figure 5.10, the presence of ethanol had varied impacts on the vapour phase transport of the gasoline compounds probably due to their differences in property. While the presence of ethanol promoted the vapour phase transport of the alkanes (pentane) and cycloalkanes (MCP) to the groundwater zone, it reduced that of the aromatics (benzene). This result has three implications. Firstly, it implies that the addition of 20% ethanol by volume to gasoline could alter the retentive capability of SOM as also observed for the microcosm experiments (see Table 5.3 in Section 5.2.3). This observation is in good agreement with the finding of Adam et al. (2002) who noted that the addition of 25% ethanol to fuel reduced the retentive behaviour of a sandy soil. According to Adam et al. (2002), this observation is expected as ethanol is known to break the surface tension of water repellent sand, allowing increased water infiltration. Secondly, it indicates that the addition of 20% ethanol by volume to gasoline is likely to have greater impact on the water phase transport of the aromatics. Finally, it suggests that less soluble gasoline compounds, such as the alkanes and cycloalkanes, which usually are of little concern, can represent a greater risk towards

groundwater contamination when high volume of ethanol is added to gasoline.

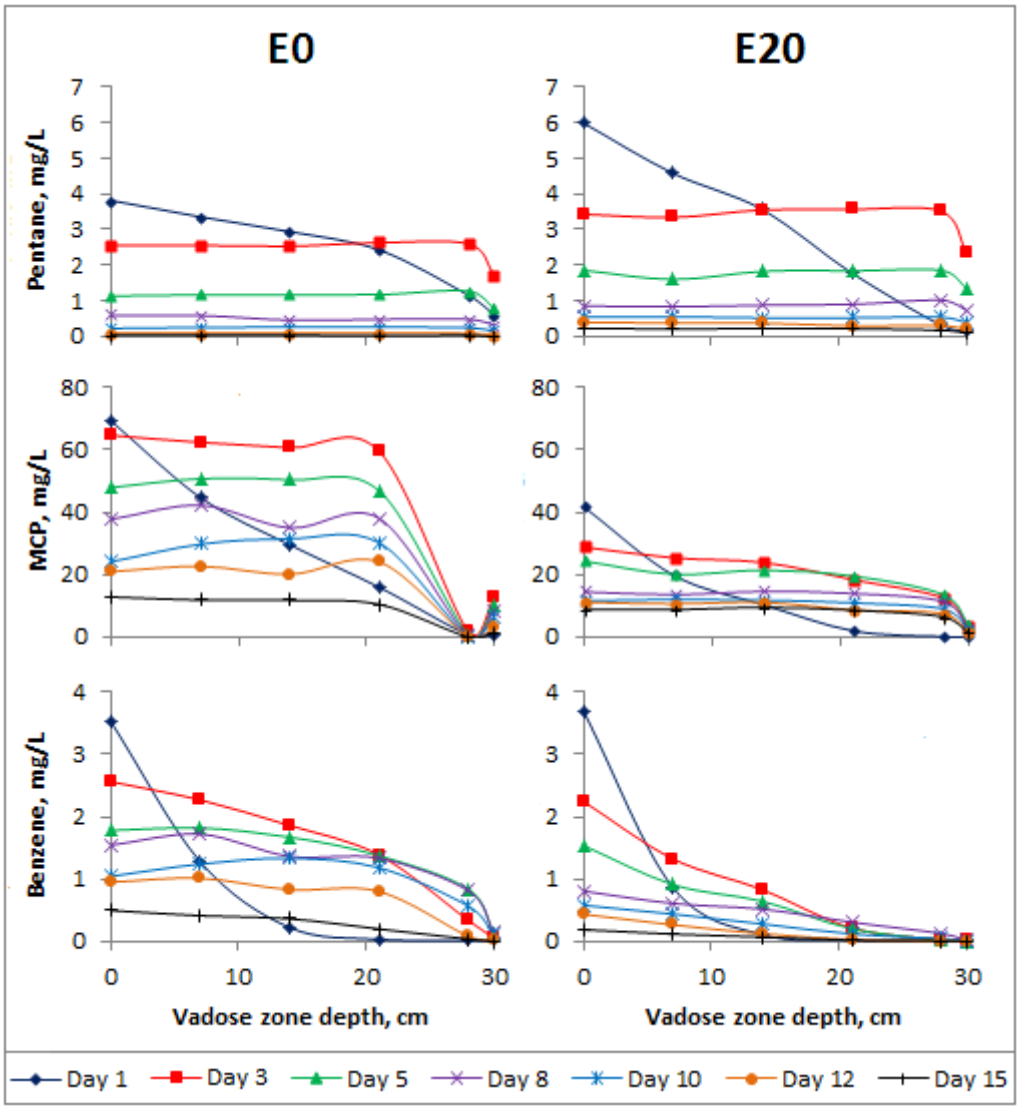

Figure 5.10 Impact of ethanol on the vapour phase transport of gasoline compounds in 5%f_{om}.

5.4 Summary of findings

The results of the ethanol-blended gasoline study indicate that the addition of 20% ethanol by volume to gasoline in attempts to reduce vehicular emissions to the atmosphere could reduce gasoline retention by soil, thus

increasing groundwater contamination with gasoline compounds, especially with the aromatics, and Figure 5.11 provides a graphic summary of these findings. The addition of SOM to sand changed the conformation of the sand to higher porosity and greater surface area soil, hence increased the sorption and mass distribution to soil solids of all E20 gasoline compounds. This impact, quantified by the average sorption coefficient (K_d) of E20 gasoline compounds, increased with decreasing hydrophobicity, hence affected the aromatics to a greater extent (K_d increased by about 7 times) than the alkanes and cycloalkanes (K_d increased by about 2 – 4 times). However, when compared with E0, the ethanol in E20 generally reduced the sorptive capability of SOM for gasoline compounds by a maximum of 76% for the cycloalkanes, 73% for the aromatics and 60% for the alkanes. Also, the sorptive capability of SOM was reduced with increasing soil water content, suggesting that the degree of E20 gasoline compounds retention in the vadose zone by SOM could differ during the dry summer and wet winter. In terms of E20 gasoline compounds transport in the subsurface, SOM promoted the vapour phase transport of the gasoline compounds to the groundwater zone. This effect was significant for the more hydrophobic gasoline compounds (alkanes and cycloalkanes), but insignificant for the less hydrophobic gasoline compounds (aromatics). This indicates that the addition of a high volume of ethanol to gasoline is likely to predominantly affect the water phase transport of the aromatics. Overall, it is concluded that the full sorptive capability of SOM for gasoline compounds is unlikely to be realised for E20 gasoline compounds. This would mean greater groundwater contamination with E20 gasoline compounds than with standard gasoline compounds even in soils with high SOM content. This behaviour of E20 is of great significance in determining its fate in soils with varying SOM and water contents.

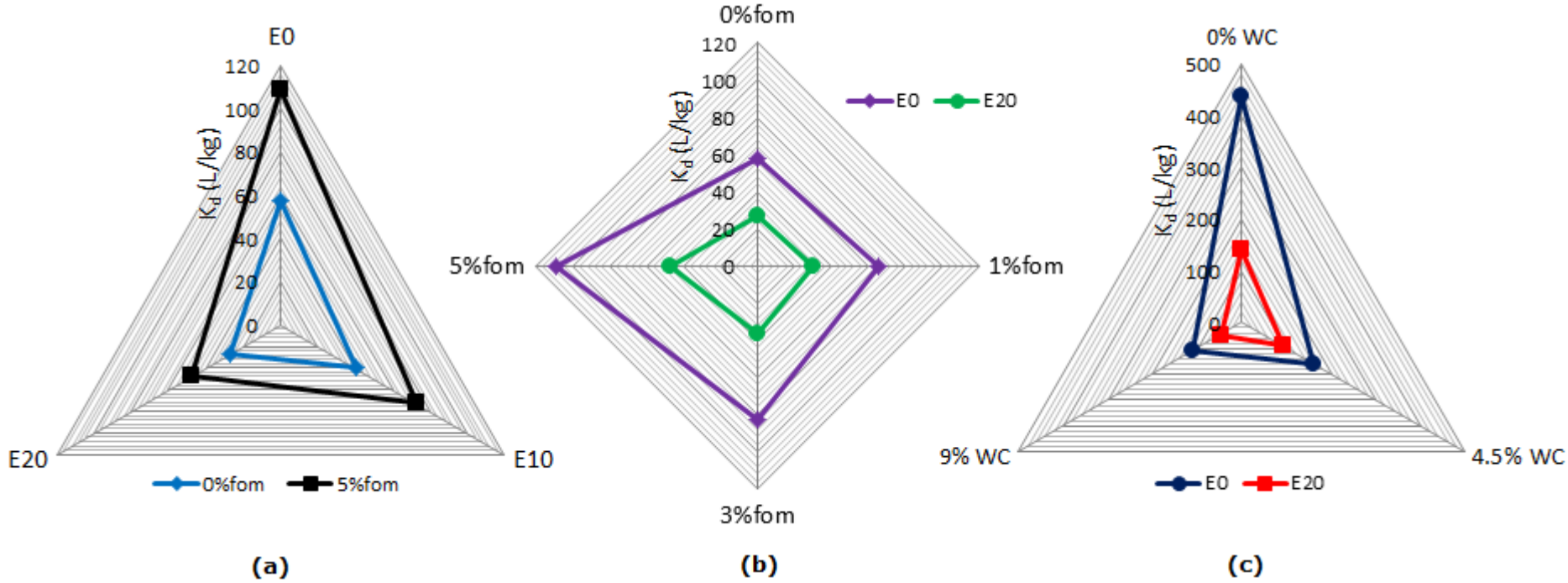

Figure 5.11 Summary of the impacts of (a) ethanol, (b) SOM and (c) soil water content on the fate of gasoline compounds in the vadose zone.

[In (c) the K_d values for 0%WC were reduced by one decimal place to accommodate the K_d values for 4.5 and 9% water content (WC)].

CHAPTER SIX

6. IMPACT OF SOM ON THE SORPTION AND TRANSPORT OF BUTANOL-BLENDED GASOLINE VAPOURS IN THE VADOSE ZONE

6.1 Introduction

Butanol has recently gained increasing interest as a gasoline oxygenate following some promising techniques for its production from renewable and cost-effective cellulosic materials (Kumar and Gayen, 2011) as well as its advantages over ethanol as discussed in Section 2.3.3. However, little is known about the impact of butanol on the sorption and transport of gasoline compounds in the vadose zone. More so, the extent to which SOM will affect the sorption and transport of butanol-blended gasoline compounds in the vadose zone has not been addressed in the literature. Knowing the sorption and transport of butanol-blended gasoline in vadose zones with varying SOM contents will be useful both in making informed decision on its use and in assessing risks of spills. A number of laboratory microcosm and mini-lysimeter experiments were performed to gain this knowledge. The results obtained are similarly presented in this chapter as those for ethanol-blended gasoline in Chapter 5.

6.2 Microcosm experiments

6.2.1 Impact of butanol on the sorption and phase distribution of gasoline compounds

6.2.1.1 Sorption of gasoline compounds

Figure 6.1 compares the changes in the headspace concentrations of B0, B10 and B20 gasoline compounds with time after injection in the microcosms as described in Section 3.3.2. The presence of butanol caused higher vapour concentrations of the gasoline compounds at the headspace of microcosms. Before equilibrium around Day 6, the headspace vapour concentrations increased with increasing volume of butanol. This higher headspace vapour concentrations indicates a lower sorption of the gasoline compounds by the soil. This lowered sorption was generally greatest 4 h after contamination on Day 1 suggesting that the cosolvent effect of butanol on gasoline compounds would be greatest on the first day of the butanol-blended gasoline spill. The sorption of the aromatics was affected to a greater extent by the presence of butanol compared with those of the alkanes and cycloalkanes, probably due to their lower hydrophobicity. The sorption of the B10 and B20 gasoline compounds were reduced by a maximum of 6 and 7% for the alkanes, 8 and 10% for the cycloalkanes and 84 and 96% for the aromatics, respectively. As explained in Section 5.2.1.1, the observed impact of butanol on the sorption of all gasoline compounds could be due to the early high butanol sorption and the associated blockage of the soil surface, while the similar equilibrium observed on Day 15 could be due to the complete partitioning of the butanol from the soil surface to the soil water. The general initial reduction in the sorption of the B10 and B20 gasoline compounds suggests that butanol-blended gasoline would be retained less in the vadose zone

compared with standard gasoline, hence could increase the risk of groundwater contamination with gasoline compounds after a spill to the vadose zone.

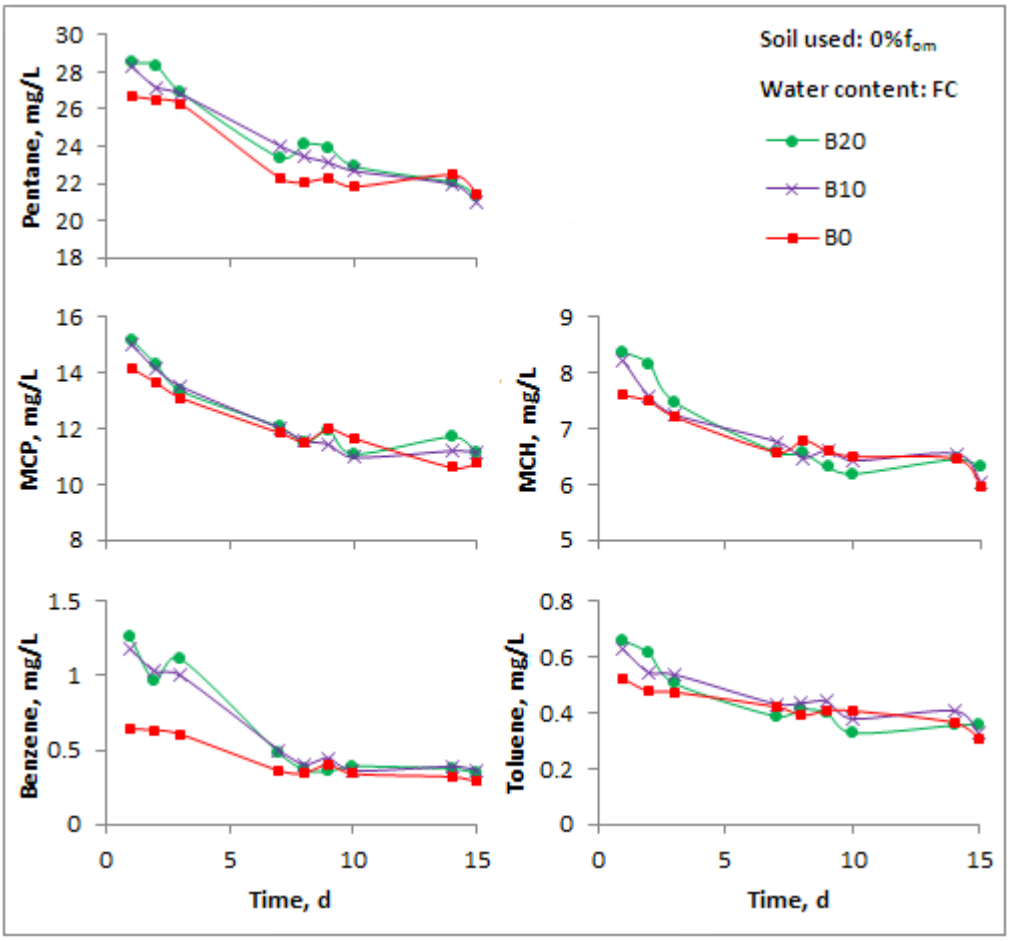

Figure 6.1 Impact of butanol on the headspace concentrations of gasoline compounds with time for 0%f_{om}.

6.2.1.2 Soil-water interaction of gasoline compounds

The impact of butanol on the average sorption coefficient (K_d) of the gasoline compounds is presented in Figure 6.2. The K_d of the butanol-blended gasoline compounds were calculated as described in Section 5.2.1.2 for the ethanol-blended gasoline compounds. The addition of butanol to gasoline reduced the K_d of all the gasoline compounds. This

effect increased with increasing volume of butanol with estimated maximum reductions of 37 and 49% for the aromatics, 22 and 39% for the alkanes and 20 and 38% for the cycloalkanes, for 10 and 20% butanol, respectively. This reduction, probably caused by reduced hydrophobicity (Powers et al., 2001b; UTTU, 2003), indicates a reduction in the mass of gasoline compounds adsorbed on the soil solids. It also indicates an increase in the mass of gasoline compounds in the soil water. Similar reduction in the K_d of hydrocarbons in the presence of other alcohols have been observed. For example, the K_d of naphthalene and phenanthrene were reported to decrease in the presence of methanol (Bouchard, 1998). In Section 5.2.1.2, the K_d of all gasoline compounds decreased with increasing volume of ethanol in gasoline. According to Powers et al. (2001b) and UTTU (2003), a reduced retention by soil solids and an increased partitioning to soil water would result in an increased flux of contaminants to the groundwater. Therefore, this result indicates that the use of butanol-blended gasoline as transportation fuel could increase the risk of groundwater contamination with gasoline compounds following a spill or leak.

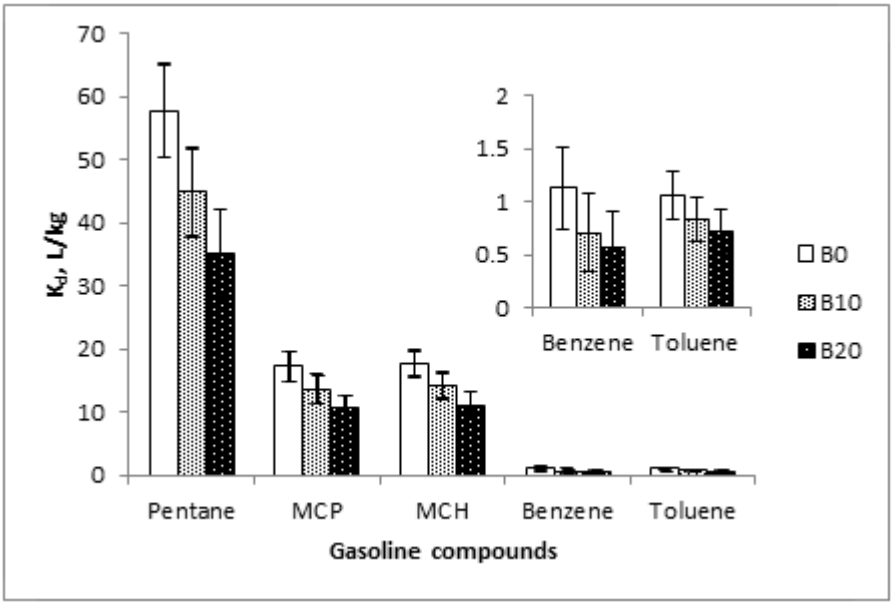

Figure 6.2 Impact of butanol on the average K_d of gasoline compounds for 0%f_{om} at field capacity.

6.2.1.3 Mass distribution of gasoline compounds between vadose zone phases

Table 6.1 presents the mass distribution of B0 - B20 gasoline compounds between the soil water, soil air and soil solid phases for 0%f_{om} at field capacity. The presence of butanol increased the mass of gasoline compounds in the mobile phases (soil water and soil air), but reduced the mass in the immobile soil solid phase. This effect increased with increasing volume of butanol and was generally greatest on Day 1. Among the gasoline compounds, the aromatics were affected to a greater extent than the other gasoline compounds. The estimated percentage of benzene, the aromatics representative compound, in the soil air at equilibrium for the butanol-blended gasoline was 8.4 to 9.4% and compares well with the 11.1% reported for sandy soil by Dakhel et al. (2003). The slight difference is assumed to be due to the difference in fuel composition. This effect of fuel composition can also be seen in the benzene soil air mass of 11.2% for

E20 in Section 5.2.1.3 as compared to the benzene soil air mass of 9.4% for B20. Generally, the observed mass decrease in the immobile phase as well as the mass increase in the mobile phases with the presence of butanol implies reduced retention of gasoline compounds in the vadose zone and increased migration of gasoline compounds to the groundwater. Therefore, the addition of 10 and 20% butanol by volume to gasoline could increase the risk of groundwater contamination, more especially with the less hydrophobic gasoline compounds, such as the aromatics.

Table 6.1 Impact of 10 and 20% butanol by volume on the mass distribution of gasoline compounds between 0%f_{om} vadose zone phases.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	B0	**B10**	**B20**	**B0**	**B10**	**B20**	**B0**	**B10**	**B20**	**B0**	**B10**	**B20**	**B0**	**B10**	**B20**
Mass in soil water, %															
1	0.1	0.2	0.2	0.4	0.5	0.6	0.4	0.5	0.6	10.8	23.0	28.9	8.8	12.2	14.9
8	0.1	0.1	0.2	0.4	0.4	0.5	0.3	0.4	0.5	6.8	7.9	8.5	8.1	8.5	9.4
15	0.1	0.1	0.1	0.3	0.4	0.5	0.3	0.4	0.4	4.9	7.1	7.9	5.2	6.3	8.1
Mass in soil air, %															
1	33.6	41.1	48.3	33.5	41.0	48.2	35.1	43.7	52.1	12.8	27.1	34.1	12.2	16.8	20.7
8	28.1	34.1	40.8	28.4	31.6	36.5	30.5	34.5	40.8	8.1	9.3	10.0	11.2	11.7	13.0
15	27.0	30.5	32.8	25.5	30.5	35.3	27.6	32.1	39.3	5.7	8.4	9.4	7.2	8.7	11.3
Mass in soil solids, %															
1	66.3	58.8	51.6	66.1	58.5	51.1	64.5	55.8	47.3	76.4	50.0	37.0	79.1	71.0	64.4
8	71.7	65.5	58.7	71.1	67.8	62.9	69.0	64.8	58.4	85.0	82.7	81.3	80.7	79.7	77.6
15	72.5	69.0	60.6	73.9	68.7	63.7	71.7	67.2	59.7	89.3	84.4	82.5	87.5	84.7	80.4

All experiments were conducted using 0%f_{om} at FC

6.2.2 Impact of SOM on the sorption and phase distribution of B20 gasoline compounds

6.2.2.1 Sorption of B20 gasoline compounds

Figure 6.3 presents the concentrations of B20 gasoline compounds in the headspace of the microcosms with time as a function of SOM fraction of the soils. The headspace concentration of all the different gasoline compounds decreased with time, albeit at different rate. All gasoline compounds attained equilibrium within the 15 days duration of the experiment, except for pentane that still maintained an approximate linear decrease in concentration with time at that point. The decrease in the headspace concentration of the gasoline compounds indicates increase in sorption to the soil.

The increase in the SOM fraction of soils resulted in greater sorption of all compounds. This enhanced sorption of compounds by SOM could be due to the increased porosity, surface area and total pore volume of soils with increasing SOM fraction as listed in Table 4.4 in Section 4.3. The ethanol-blended gasoline study in Chapter 5 (Section 5.2.2.1) indicated that SOM had no significant impact on the sorption of ethanol. Therefore, the impact of SOM on the sorption of butanol confirmed that butanol has lower water absorption than ethanol, as published by the United States Environmental protection Agency (USEPA, 2005), and higher octanol-water partition coefficient (K_{ow}) as reported by Yaws (2008). Consequently, butanol is likely to have less adverse effect, compared with ethanol, on the sorption of gasoline compounds by SOM.

Among the gasoline compounds, SOM impacted the sorption of the aromatics to a greater extent of 75 to 81% than the cycloalkanes of 50 to 61% and the alkanes of 32%. Previous studies on sorption have shown that variation in the sorption of organic compounds by soils could be due to competitive sorption resulting from the differences in sorption energies and/or site limitations, the quality and quantity of the adsorbent, and the co-solute concentrations (Allen-King et al., 2002; Pignatello et al., 2006; Weber Jr et al., 1991). In this study, the competitive sorption of gasoline compounds resulting from their difference in C-C bond lengths seemed to be the dominant factor affecting sorption by SOM as earlier stated in Section 5.2.2.1. Overall, this result indicates that SOM promoted the sorption of all B20 gasoline compounds. This effect was greater on the aromatics than on the cycloalkanes and alkanes.

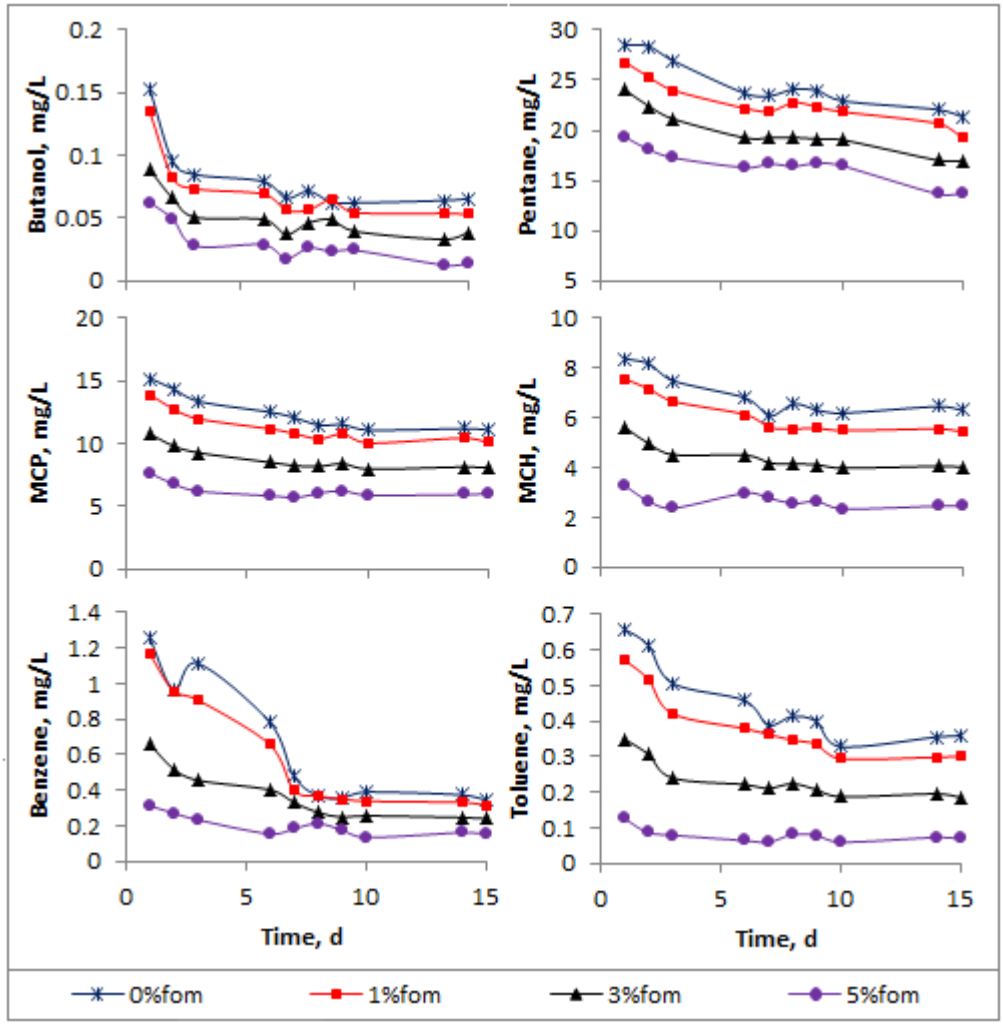

Figure 6.3 Headspace concentrations of B20 gasoline compounds with time as a function of SOM fraction of soils.

6.2.2.2 Soil-water interaction of B20 gasoline compounds

Figure 6.4 shows the impact of SOM on the average sorption coefficient (K_d) of B20 gasoline compounds in the vadose zone. The K_d values obtained are comparable to those reported in the literature for standard gasoline as stated in Section 5.2.2.2. Compared with the K_d values obtained for the E20 gasoline compounds, higher K_d values were obtained for the B20 gasoline compounds, which suggests that butanol may have less adverse effects on the adsorption of gasoline compounds than ethanol. The K_d values for all gasoline compounds increased with increasing SOM

fraction (f_{om}) of the soils. This indicates an increase in the adsorption of gasoline compounds on soil solids and/or decrease in the dissolution of gasoline compounds into the soil water. Like the ethanol-blended gasoline study (Section 5.2.2.2), the impact of SOM was greatest for the aromatics where the K_d increased 7 times, compared with the 4 times for the cycloalkanes and 2 times for the alkanes, as the f_{om} increased from 0 to 5%. As noted in Section 5.2.2.2, this direct relationship between K_d and SOM have also been reported for a wide range of organic contaminants and adsorbents, but it is to the authors knowledge shown for the first time for butanol-blended gasoline. Thus, the data indicate that SOM increased the adsorption of B20 gasoline compounds on the soil solids, but reduced their dissolution into the soil water. This effect is likely to be greatest for the aromatics compared with the alkanes and cycloalkanes.

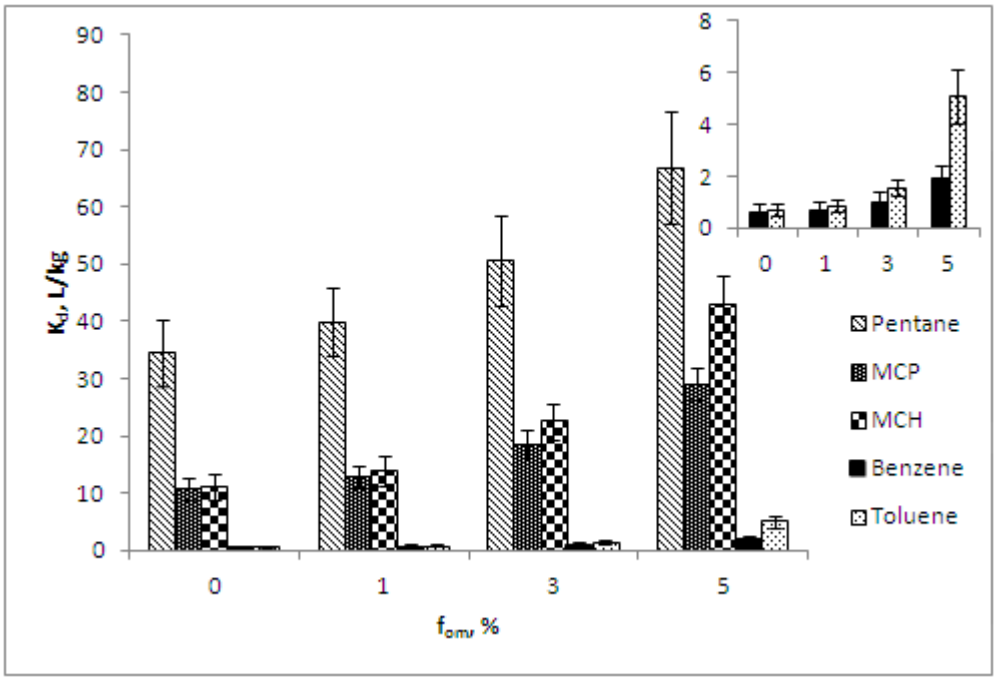

Figure 6.4 Average sorption coefficient (K_d) of B20 gasoline compounds as a function of SOM fraction of soils.

6.2.2.3 Retardation of the migration of B20 gasoline compounds

Figure 6.5 presents the impact of SOM on the retardation factor (R) of B20 gasoline compounds in the vadose zone. Generally, the R values for all gasoline compounds increased with increasing f_{om}, suggesting that partitioning into SOM is a major process causing retardation. This effect increased with increasing hydrophobicity, hence was greatest for the cycloalkanes where it increased from 0 to 64 and least for the aromatics from 0 to 9.4 as the f_{om} increased from 0 to 5%. By comparing the R values for B20 and E20 gasoline compounds, as shown in Figures 6.5 and 5.5, respectively, it was found that SOM had a higher impact on the R of B20 gasoline compounds than on the R of E20 gasoline compounds. This implies that B20 may have a slow migration in the vadose zone compared to E20 after spills. Also, a comparison of the R values obtained for the gasoline compounds in 0%f_{om}, e.g. 2.75 for benzene and 3.18 for toluene, with those reported for sandy soil by Höhener et al. (2006), 1.24 for benzene and 1.93 for toluene, and those estimated from the K_d values reported for sandy soil by Joo et al. (2008) as described in Section 5.2.2.3, 1.61 for benzene and 1.91 for toluene, showed good agreement, despite the slight contaminant mixture differences. However, the R values for benzene and toluene obtained in different soils, such as clay (Myrand et al., 1992), 117.2 for benzene and 734 for toluene, and fine silty loam (Johnson and Perrott, 1991), 193.0 for benzene and 218.0 for toluene, showed great difference from the R values obtained for 0%f_{om} in this study. These observations uphold the large influence of soil types and properties over that of the contaminant composition observed in Section 5.2.2.3. In all, the data indicate that increasing SOM reduces the migration of B20 gasoline compounds in the vadose zone. This effect is likely to increase with increasing hydrophobicity of gasoline compounds.

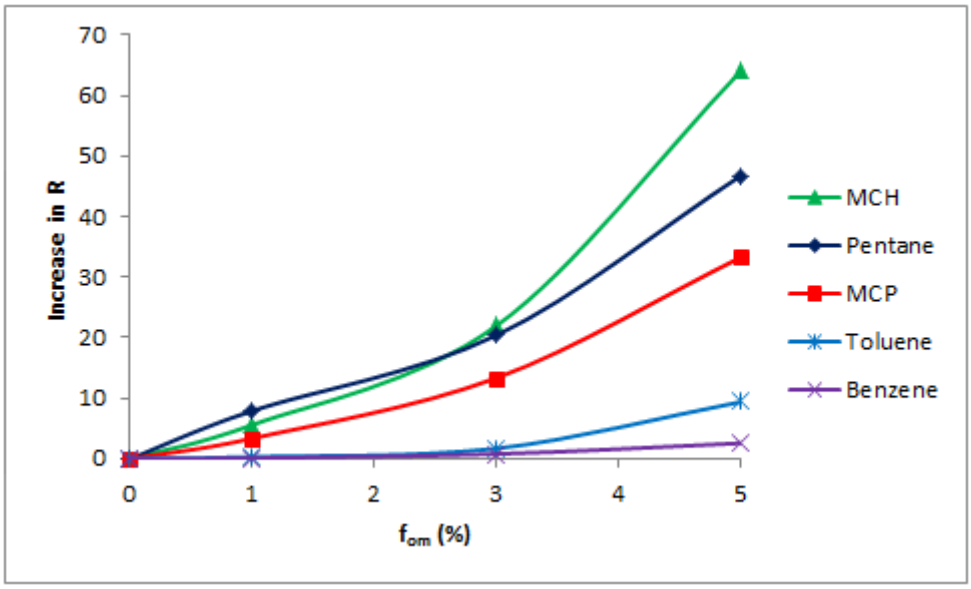

Figure 6.5 Impact of SOM on the retardation factor (R) of B20 gasoline compounds.

6.2.2.4 Mass distribution of B20 gasoline compounds between vadose zone phases

Table 6.2 lists the changing masses of B20 gasoline compounds in the soil air, soil solids and soil water with changing SOM fraction of the soils. The increase in the SOM fraction of soils resulted in an increased mass distribution of gasoline compounds to the soil solids and in a reduced mass distribution to the soil air and soil water. Although this effect was observed throughout the duration of the experiment, it was generally greatest on Day 1 and affected the aromatics to a greater extent, with a maximum increase in adsorption on soil solids of 49% for 0 to 5% increase in SOM fraction of soils, than the cycloalkanes of 35% and the alkanes of 20%. The reduction in the amount of available soil water in the microcosm with increasing SOM fraction of soils, as already explained in Section 5.2.2.4, could be the possible reason for the greater impact of SOM on the adsorption of the less hydrophobic gasoline compounds, such as the aromatics. However, on Day 15, when equilibrium is assumed to have been

reached, SOM promoted the adsorption of gasoline compounds based on hydrophobicity, with the cycloalkanes being promoted to a greater extent of 26.8% compared to the alkanes of 16.4% and the aromatics of 16.0%. This implies that the bonding forces between the dipole moments of the SOM and the aromatics may be weaker than those of the cycloalkanes and the alkanes. Hence, any aromatics retained by SOM in the vadose zone after a spill of B20 may leach out faster with time than the cycloalkanes or alkanes. Overall, the data indicate that SOM could impact the phase distribution of butanol-blended gasoline in the vadose zone. Among the gasoline compounds, the impact is likely to vary with time. While the less hydrophobic gasoline compounds may be impacted to a greater extent few hours after spills, the more hydrophobic gasoline compounds are likely to be impacted to a greater extent afterwards.

Table 6.2 Mass distribution of B20 gasoline compounds in the vadose zone as a function of SOM fraction of soils.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %	Air %	Solid %	Water %
							0%f_{om}								
1	48.3	51.6	0.2	48.2	51.1	0.6	52.1	47.3	0.6	34.1	37.0	28.9	20.7	64.4	14.9
8	40.8	58.7	0.2	36.5	62.8	0.5	40.8	58.4	0.5	10.0	81.3	8.5	13.0	77.6	9.4
15	36.2	63.2	0.1	35.3	63.7	0.5	39.3	59.7	0.4	9.4	82.5	7.9	11.3	80.4	8.1
							1%f_{om}								
1	43.9	56.0	0.2	42.7	56.8	0.6	45.5	54.0	0.5	30.7	42.5	26.8	17.4	69.6	13.0
8	37.3	62.2	0.1	31.9	67.3	0.4	33.5	65.8	0.4	9.7	81.6	8.5	10.5	81.5	7.9
15	31.5	67.9	0.1	31.1	68.0	0.4	32.8	66.4	0.4	8.3	84.2	7.3	9.2	83.8	6.8
							3%f_{om}								
1	37.6	62.2	0.2	31.6	67.9	0.4	32.3	67.3	0.4	16.6	68.2	15.2	10.2	81.9	7.9
8	30.3	69.3	0.1	24.2	75.3	0.3	24.0	75.5	0.3	7.0	86.6	6.4	6.5	88.3	5.1
15	26.6	72.9	0.1	23.8	75.4	0.3	23.2	76.1	0.3	6.1	88.3	5.6	5.4	90.3	4.2
							5%f_{om}								
1	28.0	71.9	0.1	20.7	79.0	0.3	17.4	82.4	0.2	7.3	85.5	7.2	3.4	93.7	2.9
8	23.8	75.9	0.1	16.5	83.0	0.3	13.7	86.0	0.2	5.0	90.0	4.9	2.2	95.9	1.9
15	19.9	79.6	0.1	16.4	83.1	0.3	13.2	86.5	0.2	3.6	92.7	3.6	1.9	96.4	1.6

6.2.3 Butanol-influenced changes on the impact of SOM on the sorption of gasoline compounds

The impact of butanol on the sorptive capability of SOM for gasoline compounds using the average K_d of B0, B10 and B20 gasoline compounds in $0\%f_{om}$ and $5\%f_{om}$ soils is summarised in Table 6.3. The presence of butanol caused a substantial reduction in the K_d of all gasoline compounds in both $0\%f_{om}$ and $5\%f_{om}$, signifying reduction in the amount of gasoline compounds adsorbed on the soil solids. The presence of butanol also reduced the SOM-induced increase in K_d for all gasoline compounds, implying reduction in the SOM sorptive capability for gasoline compounds. This effect increased with increasing molecular weight, thus was greatest for the cycloalkanes compared with the aromatics and alkanes. The observed butanol-influenced reduction in K_d of gasoline compounds, 21 and 37% for the alkanes, 37 and 60% for the aromatics and 38 and 66% for the cycloalkanes, was found to be lesser than the ethanol-influenced reduction, 36 and 60% for the alkanes, 43 and 73% for the aromatics and 46 and 76% for the cycloalkanes as contained in Table 5.3 in Section 5.2.3, for 10 and 20% alcohol, respectively. This implies that butanol induced lesser changes in the conformation of the SOM matrix. Generally, the reduction in the K_d and in the SOM-induced increase in K_d of gasoline compounds would mean decrease in the amount of gasoline compounds retained in the vadose zone. Therefore, the data indicate that the full sorptive capability of SOM for gasoline compounds is unlikely to be realised for B10 and B20 gasoline compounds.

Table 6.3 Impact of butanol on average K_d increase by SOM.

Gasoline blend	Compound	K_d, L/kg		Increase in K_d	
		0%f_{om}	5%f_{om}	L/kg	%
B0	Pentane	57.8	108.7	50.9	88
	MCP	17.3	57.9	40.6	235
	MCH	17.8	111.5	93.7	526
	Benzene	1.1	3.4	2.3	209
	Toluene	1.1	12.1	11.0	1000
B10	Pentane	44.9	84.9	40.0	89
	MCP	13.8	41.6	27.8	201
	MCH	14.2	72.5	58.3	411
	Benzene	0.7	2.2	1.5	214
	Toluene	0.8	7.7	6.9	863
B20	Pentane	34.5	66.8	32.3	94
	MCP	10.8	29.1	18.3	169
	MCH	11.2	43.2	32.0	286
	Benzene	0.6	1.9	1.3	217
	Toluene	0.7	5.1	4.4	629

6.2.4 Impact of soil water content on SOM sorptive capability for B20 gasoline compounds

6.2.4.1 Sorption of B20 gasoline compounds

Figure 6.6 shows the difference in the headspace vapour concentrations of B20 gasoline compounds for 0, 4.5 and 9% water contents of 5%f_{om}. Similar to the observation made for E20 in Section 5.2.4.1, the increase in the water content of 5%f_{om} increased the headspace concentrations of all B20 gasoline compounds, which signify a decrease in the sorption of gasoline compounds by the soil. As explained earlier in Section 5.2.4.1, this decrease in sorption could be due to the blockage of the high-energy sorption sites of the soil by water, thus reducing the amount of these sites

for interactions with the gasoline compounds (Serrano and Gallego, 2006). According to Joo et al. (2008), this implies that the molecules of the gasoline compounds competed less effectively with the water molecules. Although similar sorption trend were observed for B20 and E20 gasoline compounds, the sorption of the B20 gasoline compounds by $5\%f_{om}$ at all water contents were generally slightly higher than those of the E20 gasoline compounds. At 0% water content, complete sorption of all aromatics was observed three days after contamination, while the alkanes and cycloalkanes persisted at small concentrations throughout the experimental duration with a total sorption of 99.7% for the alkanes and 99.8 to 99.9% for the cycloalkanes on Day 15. At 4.5% and 9% water contents, complete sorption was not observed for any gasoline compounds throughout the experimental period. The percentages of sorption on Day 15 for 4.5% were 94.5% for the alkanes, 97.0 to 98.8% for the cycloalkanes and 99.0 to 99.6% for the aromatics, while those for 9% were 92.0% for alkanes, 93.4 to 94.8% for the cycloalkanes and 98.5 to 99.2% for the aromatics. This data, like the E20 data, indicate that the sorptive capability of the SOM of soils for gasoline compounds could be reduced with increasing soil water content. This implies that the degree of B20 retention in the vadose zone by the SOM of soils could differ during the dry and wet seasons.

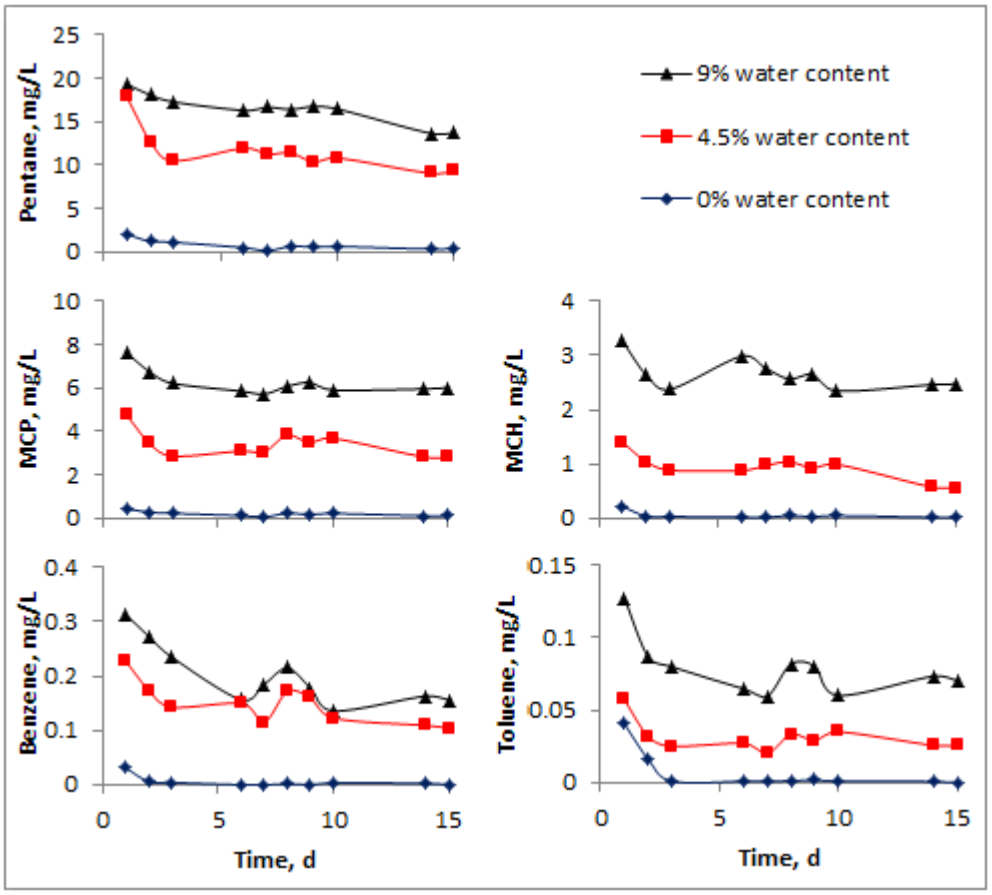

Figure 6.6 Headspace vapour concentrations of B20 gasoline compounds with time as a function of soil water content of 5%f_{om}.

6.2.4.2 Soil-water interaction of B20 gasoline compounds

Figure 6.7 presents the average K_d values for B20 gasoline compounds in 5%f_{om} wetted to 0, 4.5 and 9% water contents by weight. The K_d of all gasoline compounds decreased with increasing soil water content, implying decrease in adsorption on the SOM or increase in concentrations in the soil water. Taking 0% water content as a reference soil water content, the decrease in K_d for 4.5% water content was 95 to 98% for the aromatics, 96 to 97% for the cycloalkanes and 96% for the alkanes. In contrast, the decrease in K_d for 9% water content was 98 - 99% for all hydrocarbon groups. As explained earlier in Section 5.2.4.2, this decrease in the K_d for the B20 gasoline compounds with increasing soil water content could be

attributed to the reduction in the specific surface area of the soil by water, which in turn promoted compound-water contact. This leads to enhanced partitioning of compounds to the water phase. Therefore, similar to what was observed for E20, the increase in soil water content could decrease the sorptive capability of SOM for B20 gasoline compounds.

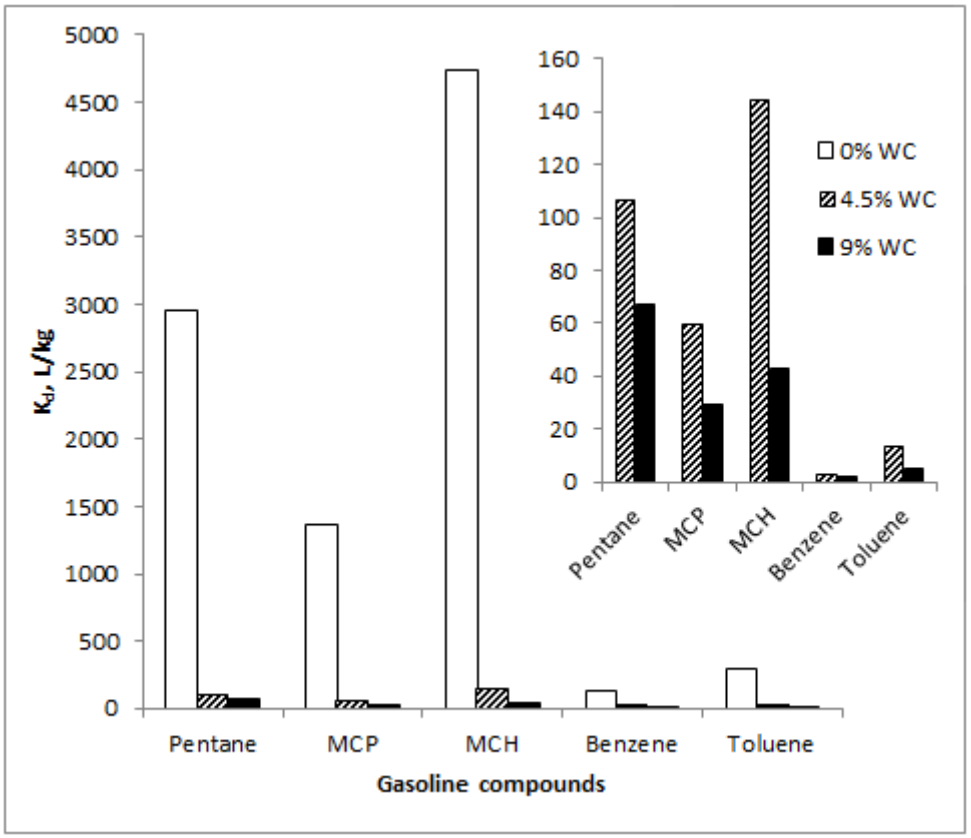

Figure 6.7 Changes in the average sorption coefficient (K_d) of B20 gasoline compounds with increasing soil water content of 5%f_{om}.

6.2.4.3 Mass distribution of B20 gasoline compounds between vadose zone phases

The changes in the mass percentages of B20 gasoline compounds in the soil water, soil air and soil solid phases of 5%f_{om} with increasing water content is presented in Table 6.4. The increase in the water content of 5%f_{om} raised the partitioning of all the B20 gasoline compounds to the soil

water and soil air, but reduced the compounds adsorption on the soil solids. Similar to E20 in Section 5.2.4.3, the increase in the partitioning of compounds to the soil water was greatest for the least hydrophobic gasoline compound, benzene, while the increase in the partitioning of compounds to the soil air was greatest for the most volatile gasoline compound, pentane. Also, the decrease in the adsorption of compounds on the soil solids was lowest for the aromatics compared to the cycloalkanes and alkanes. This reduction in the adsorption of the aromatics was attributed to lower restriction to the headspace (Section 5.2.4.3). Generally, the data show that an increase in the water content of SOM could significantly reduce its sorptive capability and thus could affect the overall mass distribution of gasoline compounds between the soil solids, soil air and soil water.

Table 6.4 Mass distribution of B20 gasoline compounds between different vadose zone phases as a function of soil water content of 5%f_{om}.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%	0%	4.5%	9%
Mass in soil water, %															
1	0	0.1	0.1	0	0.1	0.3	0	0.1	0.2	0	2.6	7.2	0	0.7	2.9
8	0	0	0.1	0	0.1	0.3	0	0	0.2	0	2.0	4.9	0	0.4	1.9
15	0	0	0.1	0	0.1	0.3	0	0	0.2	0	1.2	3.6	0	0.3	1.6
Mass in soil air, %															
1	3.3	27.0	28.0	1.3	13.5	20.7	1.3	7.8	17.4	0.8	5.5	7.3	1.2	1.6	3.4
8	1.1	17.3	23.8	0.7	10.9	16.5	0.3	5.8	13.7	0	4.2	5.0	0	0.9	2.2
15	0.6	14.2	19.9	0.4	8.0	16.4	0.1	3.1	13.2	0	2.5	3.6	0	0.7	1.9
Mass in soil solids, %															
1	96.7	72.9	71.9	98.7	86.4	79.0	98.7	92.1	82.4	99.2	91.9	85.5	98.8	97.7	93.7
8	98.8	82.5	75.9	99.2	88.9	83.0	99.6	94.1	86.0	99.9	93.8	90.0	99.9	98.6	95.9
15	99.3	85.5	79.6	99.5	91.8	83.1	99.8	96.8	86.5	99.9	96.2	92.7	99.9	98.9	96.4

0%, 4.5% and 9% are percentages of gravimetric water content of 5%f_{om}

6.3 Mini-lysimeter experiments

6.3.1 Impact of butanol on the vapour phase transport of gasoline compounds in the vadose zone

The depth profiles of vapour phase concentrations of B0, B10 and B20 gasoline compounds are shown in Figure 6.8. All the gasoline compounds diffused from the source zone (0 cm) to the groundwater zone at 28 to 30 cm within 4 h after contamination on Day 1. The presence of butanol caused a higher diffusion of all gasoline compounds to the groundwater zone probably due to the reduction in the adsorption of the gasoline compounds by the soil. This effect increased with increasing volume of butanol and was least for the heaviest representative gasoline compound (MCP) compared to the lighter compounds (pentane and benzene). This behaviour of the heaviest representative gasoline compound relative to the lighter compounds suggests that density-driven transport of compounds was not a major route. The presence of butanol also increased the vapour phase concentrations of the gasoline compounds in the vadose zone. This observation was not expected for two reasons. Firstly, the volatility of the butanol blends should be lower than that of the unblended gasoline due to the lower vapour pressure of butanol relative to the gasoline compounds as contained in Table 3.1 in Section 3.1. This should result in lower vapour phase concentration of the B10 and B20 gasoline compounds in the vadose zone. Secondly, butanol is much more soluble than the gasoline compounds. Therefore, its presence should increase the partitioning of the gasoline compounds to the water phase, which in turn should lower the vapour phase concentration of the gasoline compounds in the vadose zone. Additional research that will measure contaminants in the water phase and extract contaminants from the solid phase may be required in the future to

fully explain the reason for the increased vapour phase concentrations of the gasoline compounds in the presence of butanol in the vadose zone. Overall, the data indicate that the addition of butanol to gasoline could enhance the vapour phase transport of the gasoline compounds to groundwater possibly due to reduced adsorption of the gasoline compounds by the soil.

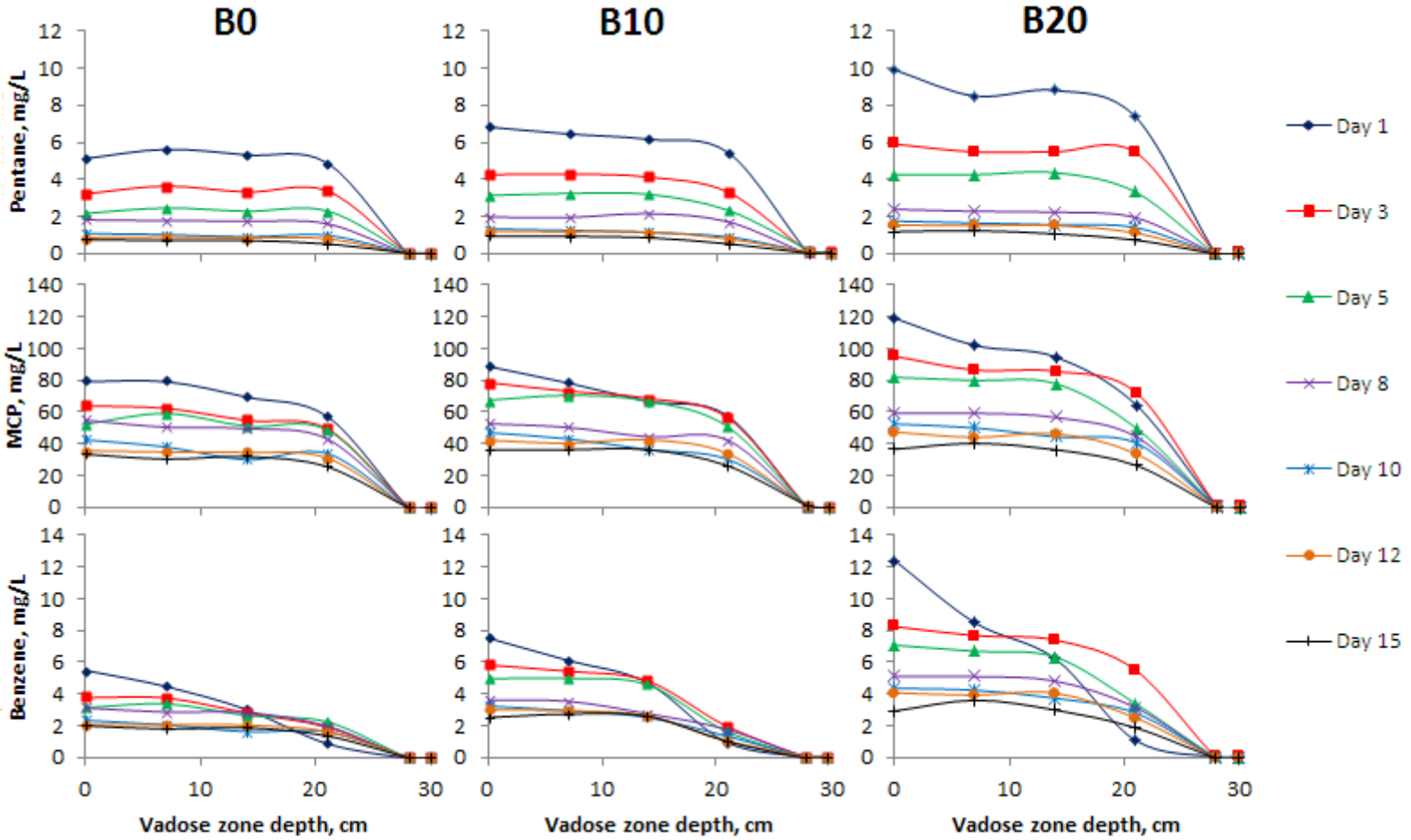

Figure 6.8 Impact of 10 and 20% butanol by volume on the vapour phase transport of gasoline compounds in 0%f_{om} vadose zone.

6.3.2 Impact of SOM on the vapour phase transport of B20 gasoline compounds

Figure 6.9 shows the vapour phase concentration profiles of B20 gasoline compounds in the vadose zone as a function of SOM fraction of the soils. The concentration profiles for 1%f_{om} and 3%f_{om} could not be added in Figure 6.9 due to space constraint but can be viewed in Appendix C. The maximum vapour concentrations of all representative gasoline compounds were found at the source zone (0 cm) on Day 1. The concentrations of all compounds decreased with time due to diffusion, adsorption and partitioning. The porosity of the soil, the volatility and hydrophobicity of the compounds and the concentration of the compounds in the mixture were the dominant factors that influenced the diffusive vapour phase transport of the gasoline compounds in the vadose zone. No compounds were found at a detectable concentration at the groundwater zone at 28 to 30 cm for the 0%f_{om} soil, which had a porosity of 40%, except for butanol that had the lowest hydrophobicity. This suggests that the interaction of the compounds with the soil was mainly hydrophobic interactions. In contrast, 4 h after contamination on Day 1 all compounds, except for benzene with the lowest concentration in the B20 mixture, were detected at the groundwater zone of the 5%f_{om}, which had a porosity of 47%. For all SOM fractions tested, the concentration of butanol measured at the groundwater zone was higher than the other compounds, suggesting that the transport of butanol was less retarded at high SOM fractions.

Huge difference was generally observed in the behaviour of compounds when the SOM increased from 0% to 5% on all the selected days shown. For example, butanol was above detection limit at all sections for the vadose zone with 0%f_{om} soil on all days except on Day 15. However,

butanol was only above detection limit on Day 1 for the 5%f_{om} vadose zone. This sudden disappearance of the butanol from the vapour phase in the vadose zone for the 5%f_{om} soil was attributed to greater partitioning to the water phase due to the higher soil water retained by the 5%f_{om} (see Section 4.4.1) as well as the lower vapour phase concentration measured at the groundwater zone compared with 0%f_{om}. For the hydrophobic gasoline compounds, greater vapour phase transport to the groundwater zone was observed in the 5%f_{om} vadose zone. Consequently, the concentrations of all compounds at all the vadose zone sections were approximately halved for the 5%f_{om} soil compared with the 0%f_{om} soil. The higher water absorption capacity and porosity of the 5%f_{om} compared with 0%f_{om} at FC may be the reason for the observed difference in compounds behaviour in the two soils. The migration to the groundwater zone of the hydrophobic gasoline compounds increased with increasing volatility. The horizontal concentration profile of pentane in the 5%f_{om} soil on Day 3 as compared to the downward curved concentration profiles of MCP and benzene suggests a faster migration of pentane.

Overall, the vapour phase concentrations of all compounds were drastically reduced in the 5%f_{om} vadose zone compared with the vapour phase concentrations measured in the 0%f_{om} vadose zone. This reduction was attributed to higher partitioning to the soil water for butanol and to greater vapour phase transport to the groundwater zone for the gasoline compounds. The differences in the 0%f_{om} and 5%f_{om} vadose zones were attributed to the differences in the water absorption capacity and porosity of the 0%f_{om} and 5%f_{om} soils. SOM affected the vapour phase transport of B20 gasoline compounds with increasing volatility.

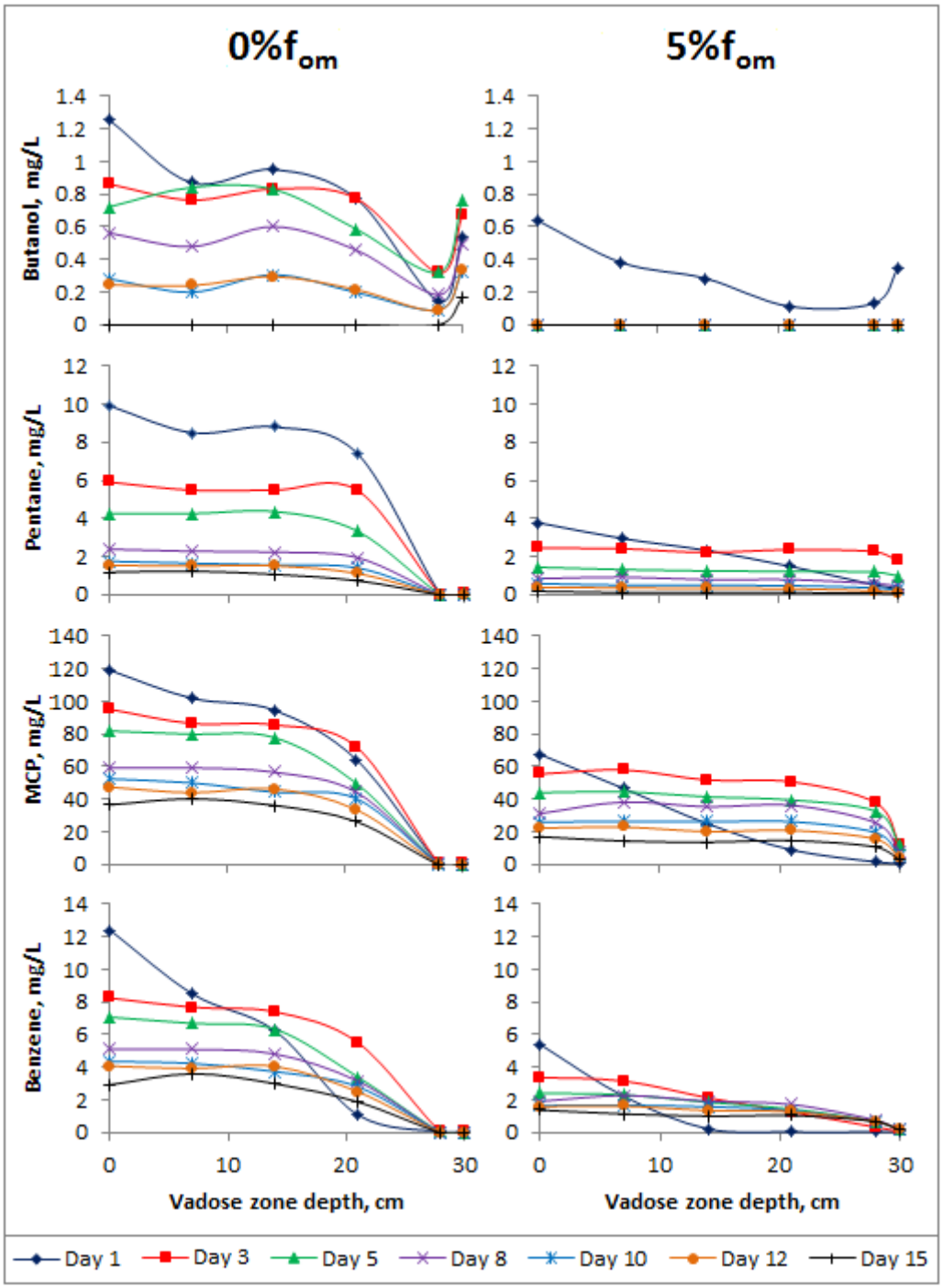

Figure 6.9 Vadose zone depth profiles of vapour phase concentrations of B20 gasoline compounds as a function of SOM fraction of soils.

6.3.3 Butanol-influenced changes on the impact of SOM on the vapour phase transport of gasoline compounds

The vapour phase concentration profiles of B0 and B20 gasoline compounds in the 5%f_{om} vadose zone are shown in Figure 6.10. The concentration profiles are shown for selected days that cover the experimental period. The high porosity of 5%f_{om} resulted in a rapid diffusive transport of all gasoline compounds from the source zone to the groundwater zone. The presence of butanol increased the diffusive transport and the vapour phase concentration of the B20 gasoline compounds in the groundwater zone. This indicates a reduction in the retentive capability of SOM for gasoline compounds vapours and, implies greater risk of groundwater contamination with B20 gasoline compounds. The higher vapour phase concentration of the B20 gasoline compounds in the groundwater zone started on Day 1 for benzene and on Day 5 for pentane and MCP. This suggests that the impact of butanol on the transport of the aromatics is likely to be significant starting from the first day of B20 spill. This further implies that the aromatics would be more likely to increase the risk of groundwater contamination than the alkanes and cycloalkanes in the presence of butanol. The increase in the vapour phase accumulation of gasoline compounds in the groundwater zone due to the presence of butanol increased with time for benzene, but decreased with time for pentane and MCP. This implies that the impact of butanol on the transport of the alkanes and cycloalkanes may persist for a shorter time than those of the aromatics. Thus, the data indicate that the addition of 20% butanol by volume to gasoline could reduce the retentive capability of SOM for gasoline compounds vapours and could lead to greater downward transport and higher accumulation of gasoline compound

vapours in the groundwater. This effect is likely to impact the gasoline compounds in the order of aromatics>cycloalkanes>alkanes.

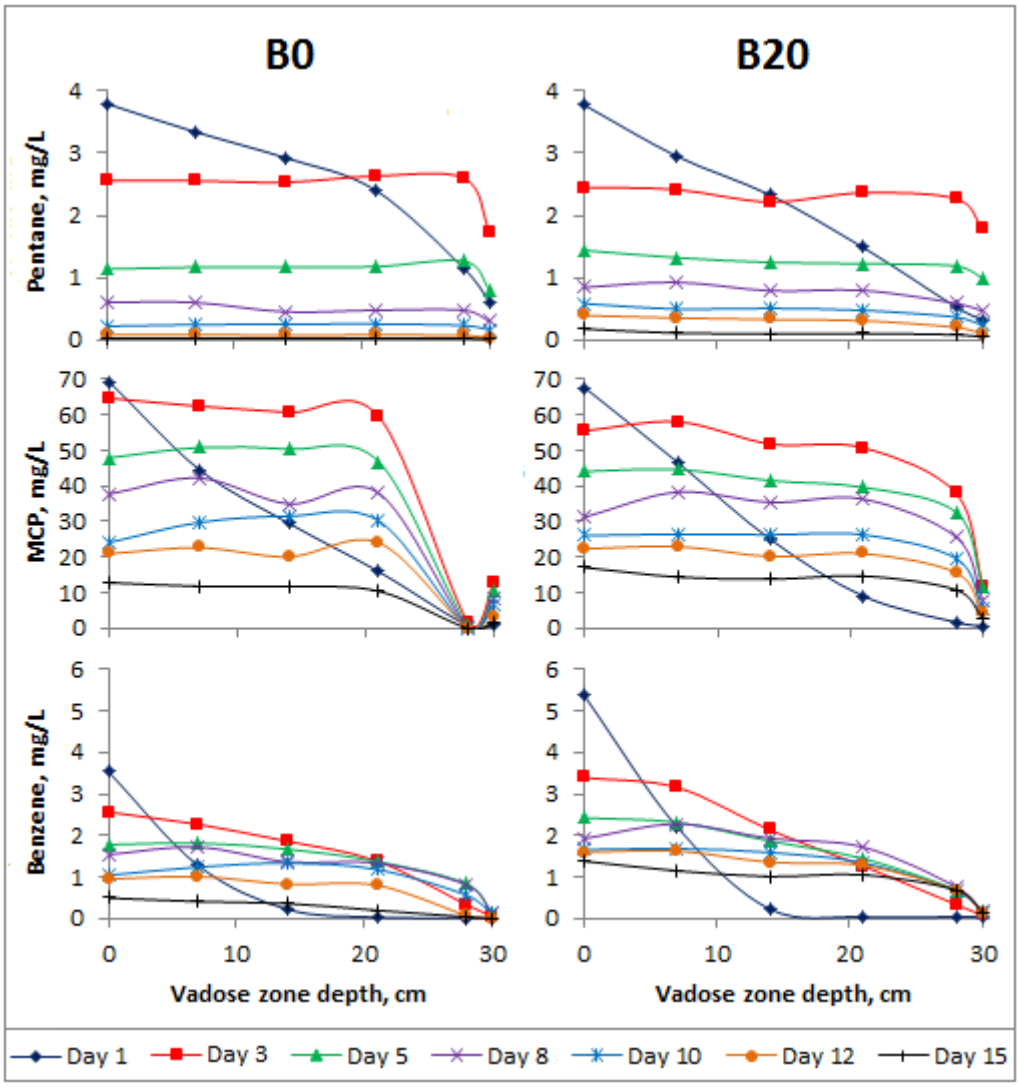

Figure 6.10 Impact of butanol on the vapour phase transport of gasoline compounds in 5%f_{om}.

6.4 Summary of findings

Figure 6.11 provides a graphic summary of the findings of the butanol-blended gasoline study. The addition of butanol to gasoline had a cosolvent effect on the gasoline compounds and caused a reduction in the sorption of

the gasoline compounds by soils. This effect is more likely to be greatest on the first day of butanol-blended gasoline spills and could affect the aromatics to a greater extent, with a K_d reductions of 37 and 49% for the aromatics, 22 and 39% for the alkanes and 20 and 38% for the cycloalkanes, for 10 and 20% butanol, respectively.

SOM showed a great impact on the sorption and phase distribution of B20 gasoline compounds in the vadose zone. For a 5% increase in SOM fraction of sand, the K_d of the B20 gasoline compounds increased by about 7 times for the aromatics, 4 times for the cycloalkanes and 2 times for the alkanes. However, the sorptive capability of SOM for B20 gasoline compounds was found to be reduced by 66% for the cycloalkanes, 60% for the aromatics and 37% for the alkanes relative to B0 gasoline compounds. This implies that the use of high volume of butanol in gasoline to combat climate change is likely to reduce the retentive capability of SOM, thus increasing the risk of groundwater contamination with gasoline compounds. Furthermore, the sorptive capability of SOM was reduced with increasing soil water content, which indicates that the degree of compounds retention in the vadose zone by SOM could differ for the dry and wet seasons.

The addition of SOM to sand increased the porosity of the resulting soil and thus promoted the vapour phase transport of gasoline compounds to the groundwater zone. SOM impacted the vapour phase transport of gasoline compounds with increasing volatility. The addition of 20% butanol by volume to gasoline reduced the retentive capability of SOM for gasoline compound vapours and thus resulted in greater downward transport and higher accumulation of gasoline compounds in the groundwater zone. This effect is likely to affect the gasoline compounds in the order of aromatics>cycloalkanes>alkanes.

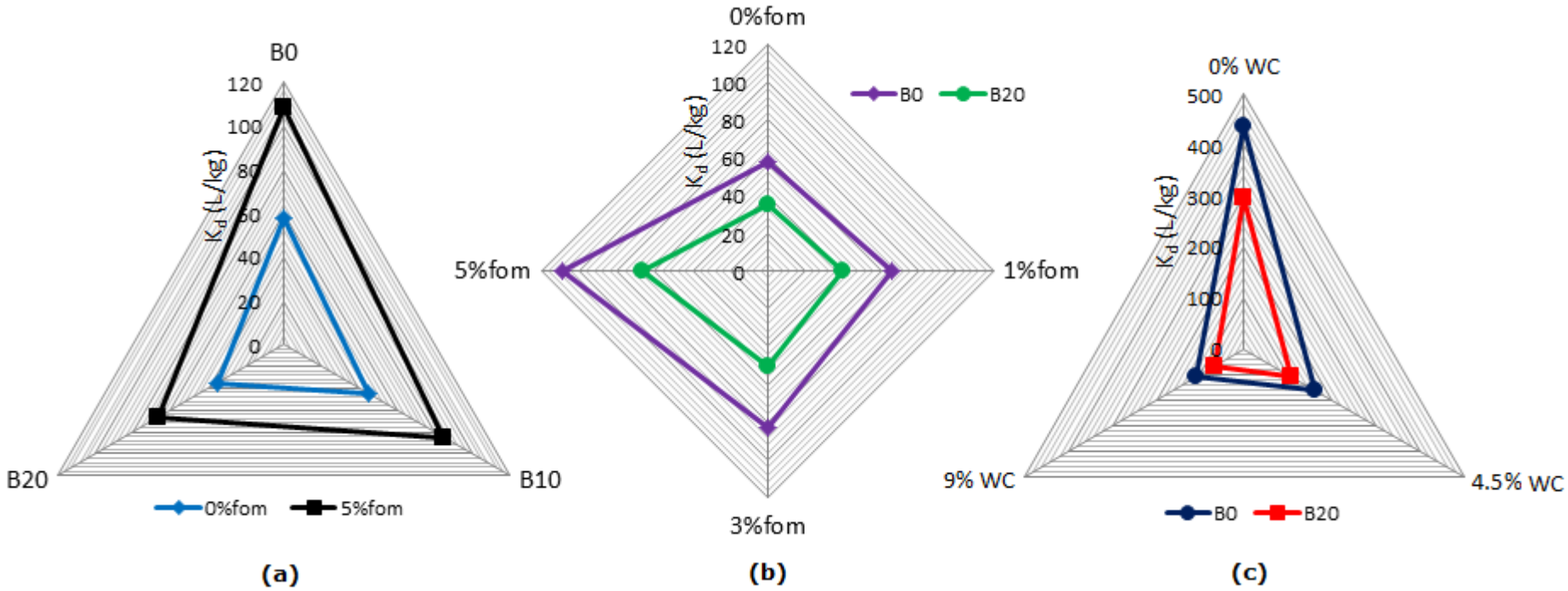

Figure 6.11 Summary of the impacts of (a) butanol, (b) SOM and (c) soil water content on the fate of gasoline compounds in the vadose zone.

[In (c) the K_d values for 0%WC were reduced by one decimal place to accommodate the K_d values for 4.5 and 9% water content (WC)].

CHAPTER SEVEN

7. MIGRATION RISKS IN SOILS DERIVED FROM THE COMPARISON OF THE SORPTION AND TRANSPORT OF E20 AND B20 VAPOURS

7.1 Introduction

The migration risks in soil for E20 and B20 vapours have been compared based on their sorption and transport behaviours in the vadose zone following a release. This comparison is necessitated to ascertain the gasoline blend that poses a greater risk of groundwater contamination after a spill or leak. In all comparison cases, the unblended gasoline (UG) was used as the benchmark.

7.2 Microcosm experiments

7.2.1 Impact of SOM on the sorption and phase distribution of different gasoline blends

7.2.1.1 Sorption of gasoline compounds

Figure 7.1 compares the headspace concentrations of selected gasoline compounds for UG, E20 and B20 with increasing SOM fractions of the soil. The three gasoline compounds shown are the representatives of the three hydrocarbon groups constituting the synthetic gasoline mixture. Selection of the representative gasoline compounds was necessary to reduce congestion of figure, and was based on volatility. The headspace concentrations of all compounds for all three fuels decreased with time,

signifying the increase in sorption to the soil. The addition of 20% alcohol by volume to gasoline reduced the sorption of all gasoline compounds due to the early high alcohol sorption and the associated blockage of the soil surface as explained earlier in Sections 5.2.1.1 and 6.2.1.1. This reduction was generally greater on Day 1 and affected the E20 gasoline compounds to a greater extent compared to the B20 gasoline compounds. This suggests that the use of E20 as transportation fuel could result in greater groundwater contamination with gasoline compounds than the use of B20, and that the difference in groundwater contamination is likely to be greatest on the first day of spill. Compared with the sorption of the UG gasoline compounds by the 0%f_{om} soil, the reductions in the sorption of the E20 gasoline compounds were 28% for pentane, 25% for MCP and 91% for benzene, while the reductions in the sorption of the B20 gasoline compounds were 7% for pentane, 7% for MCP and 96% for benzene. Although the sorption of benzene from B20 seemed to be reduced to a greater extent than the benzene from E20 on Day 1, the reductions on the subsequent experimental days, when equilibrium had been attained, were clearly higher for E20. For example, on Day 8 the reduction in the sorption of benzene was 38% for E20 and 7% for B20, and on Day 15 it was 25% for E20 and 20% for B20.

The increase in the SOM fraction of soils resulted in a rapid and greater sorption for all the gasoline compounds. This increase in sorption suggests a reduction in groundwater contamination with gasoline compounds. The impact of SOM on the sorption of gasoline compounds varied with gasoline composition. Generally, SOM promoted the sorption of the B20 gasoline compounds to a greater extent compared to the sorption of the E20 gasoline compounds. This implies that the increase in the SOM content of soils may generally reduce the groundwater contamination with B20

gasoline compounds to a greater extent than the groundwater contamination with E20 gasoline compounds. On Day 1 after contamination, when the effect of SOM on sorption was generally greatest, the sorption of B20 gasoline compounds was increased by 32% for pentane, 50% for MCP and 75% for benzene, while the sorption of E20 gasoline compounds was increased by 29% for pentane, 46% for MCP and 76% for benzene, for 5% increase in the SOM fraction of a sand. The similar increase in the sorption of benzene by SOM suggests that butanol and ethanol may have similar cosolvent effect on benzene.

Another interesting impact of the SOM on the sorption of gasoline compounds was the persistent difference in the equilibrium concentration of the gasoline compounds for the different gasoline blends. As the SOM fraction of the sand increases, the discrepancies amongst the equilibrium concentrations of the gasoline compounds from the different gasoline blends were not eliminated. Therefore, it is likely that the difference in groundwater contamination potential between B20 and E20 cannot be eliminated even at high SOM containing soils.

In general, the data show that the addition of 20% alcohol by volume to gasoline in attempts to reduce vehicular emissions to the atmosphere could reduce the sorption of gasoline compounds by soils and thus increase the risk of groundwater contamination with gasoline compounds. This impact is likely to be greater for ethanol-blended gasoline than butanol-blended gasoline. Although soils with high SOM content could significantly reduce the degree of groundwater contamination, the difference in groundwater contamination potential between ethanol-blended gasoline and butanol-blended gasoline is unlikely to be eliminated.

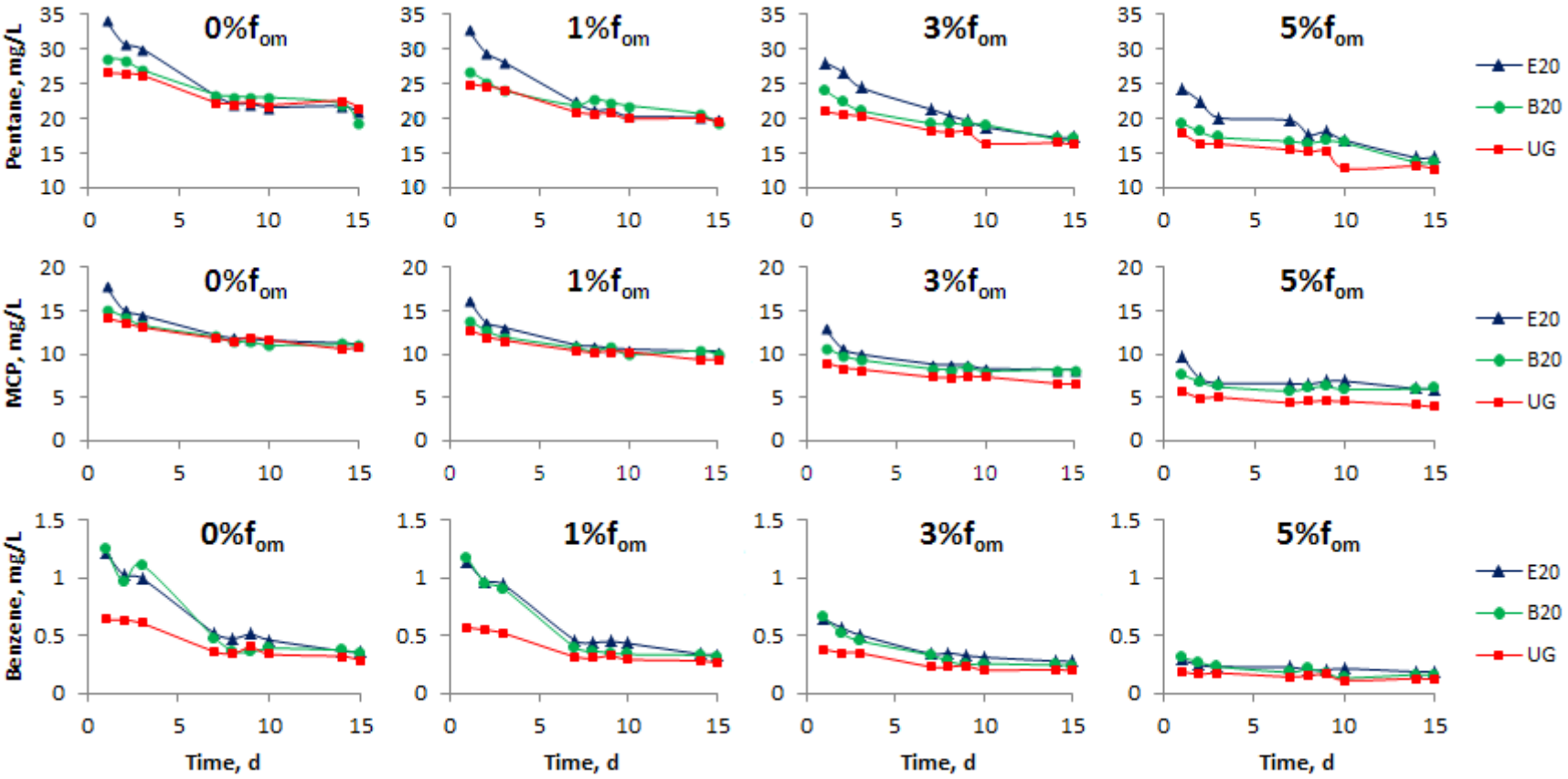

Figure 7.1 Headspace concentrations of gasoline compounds with increasing SOM fraction of soils as a function of gasoline composition.

7.2.1.2 Soil-water interaction of gasoline compounds

Figure 7.2 shows the effect of SOM on the average sorption coefficient (K_d) of representative gasoline compounds as a function of gasoline composition. The addition of alcohol to gasoline generally reduced the K_d of all gasoline compounds, suggesting a decrease in the adsorption of gasoline compounds on the soil solids and/or increase in the dissolution of gasoline compounds into the soil water. This impact was greater for the E20 gasoline compounds than for the B20 gasoline compounds, implying that the E20 gasoline compounds will have a higher percentage in the mobile water phase which in turn will result in greater groundwater contamination (Yu, 1995). Compared with the K_d of UG gasoline compounds in 0%f_{om}, the K_d of B20 gasoline compounds were reduced by 39% for pentane, 38% for MCP and 49% for benzene, while the K_d of E20 gasoline compounds decreased by 54% for pentane, 54% for MCP and 63% for benzene.

The K_d of all the gasoline compounds increased with increasing SOM fraction (f_{om}) of soils, suggesting an increase in the adsorption of all gasoline compounds on the soil solids and/or decrease in the dissolution of all gasoline compounds into the soil water. Although the K_d of E20 and B20 gasoline compounds were similarly increased by 7 times for aromatics, 4 times for cycloalkanes and 2 times for alkanes, for 0 to 5% increase in f_{om} as already presented in Sections 5.2.2.2 and 6.2.2.2, the K_d of the B20 gasoline compounds were generally greater than those of the E20 gasoline compounds for all the SOM fractions tested. More so, when compared with the K_d of UG gasoline compounds, the K_d of B20 and E20 gasoline compounds in 1%f_{om}, 3%f_{om} and 5%f_{om} were generally reduced with a trend similar to the reduction for the 0%f_{om} soil as stated in the preceding

paragraph. This may have two implications. Firstly, it suggests that groundwater contamination with gasoline compounds will always be higher for alcohol-blended gasoline than for alcohol-free gasoline regardless of the SOM content of soils. Secondly, it strengthened the observation in Section 7.2.1.1 that the difference in groundwater contamination potential between B20 and E20 cannot be eliminated by SOM.

In all, the soil-water interaction data indicate that the addition of 20% alcohol by volume to gasoline could reduce the adsorption of gasoline compounds onto the soil solids. This reduction is likely to be greater for the E20 gasoline compounds than for the B20 gasoline compounds, indicating a greater risk of groundwater contamination for E20 than for B20. However, the increase in the SOM fraction of soils could improve the adsorption of alcohol-blended gasoline compounds on the soil solids. This effect is likely to be greater for B20 than E20.

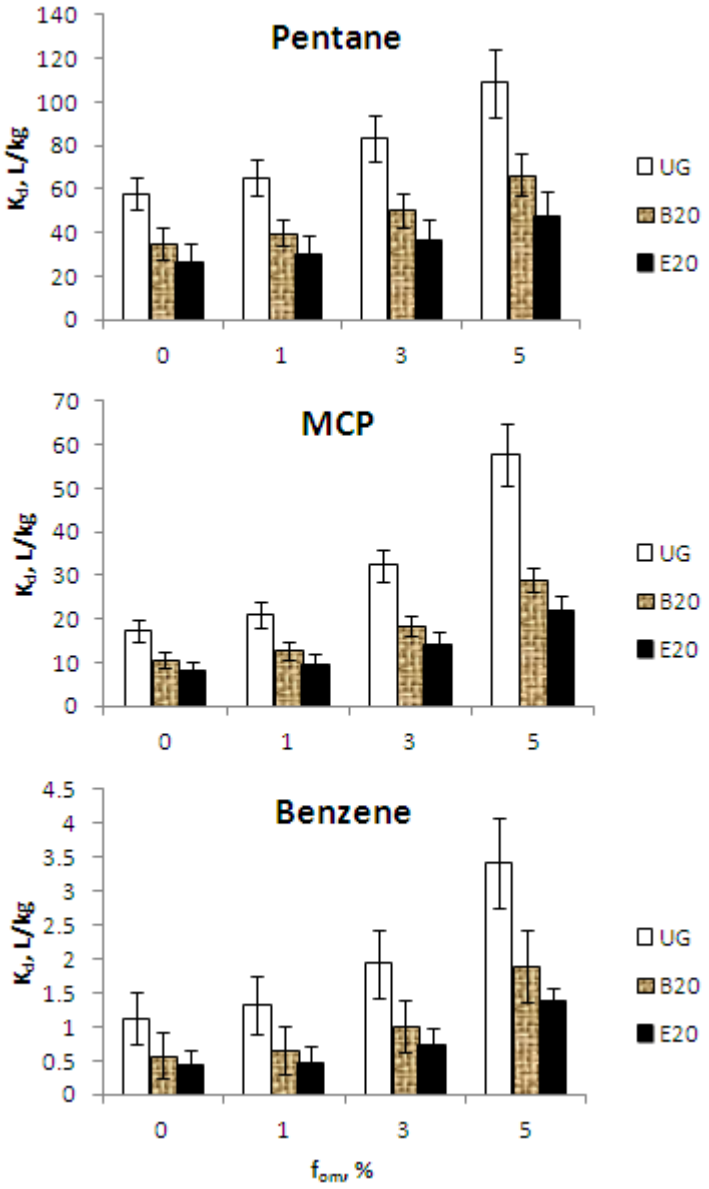

Figure 7.2 Average sorption coefficient (K_d) of gasoline compounds with increasing SOM fraction of soils as a function of gasoline composition.

7.2.1.3 Retardation of the migration of gasoline compounds

The impact of SOM on the retardation of the migration of gasoline compounds quantified by the retardation factor (R) for different gasoline blends is presented in Figure 7.3. As expected, the addition of alcohol to gasoline caused a reduction in the R values for all representative gasoline compounds. This reduction was greater for the E20 gasoline compounds

than for the B20 gasoline compounds, suggesting that the migration of the E20 gasoline compounds in the vadose zone would be retarded lesser than the migration of the B20 gasoline compounds after spills. The addition of alcohol to gasoline reduced the R values for B20 gasoline compounds in $0\%f_{om}$ by 39% for pentane, 37% for MCP and 38% for benzene, while it reduced the R values for E20 gasoline compounds by 53% for pentane, 53% for MCP and 48% for benzene.

Generally, the increase in the SOM fraction of soils increased the R values for all the gasoline compounds, implying a reduction in the migration of gasoline compounds in the vadose zone. Similar to R values in $0\%f_{om}$, the R values for all gasoline compounds in $1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$ were in the order of UG>B20>E20, indicating that the migration of E20 gasoline compounds would be retarded the least regardless of the SOM content of soils.

This result has shown that the addition of alcohol to gasoline could reduce the retardation of gasoline compounds thereby promoting migration to groundwater. This impact is likely to be greater when ethanol is added to gasoline than when butanol is added to gasoline. By increasing the SOM content of soils, the retardation of B20 and E20 gasoline compounds could be improved. However, the order of migration between B20 and E20 is unlikely to be altered by SOM.

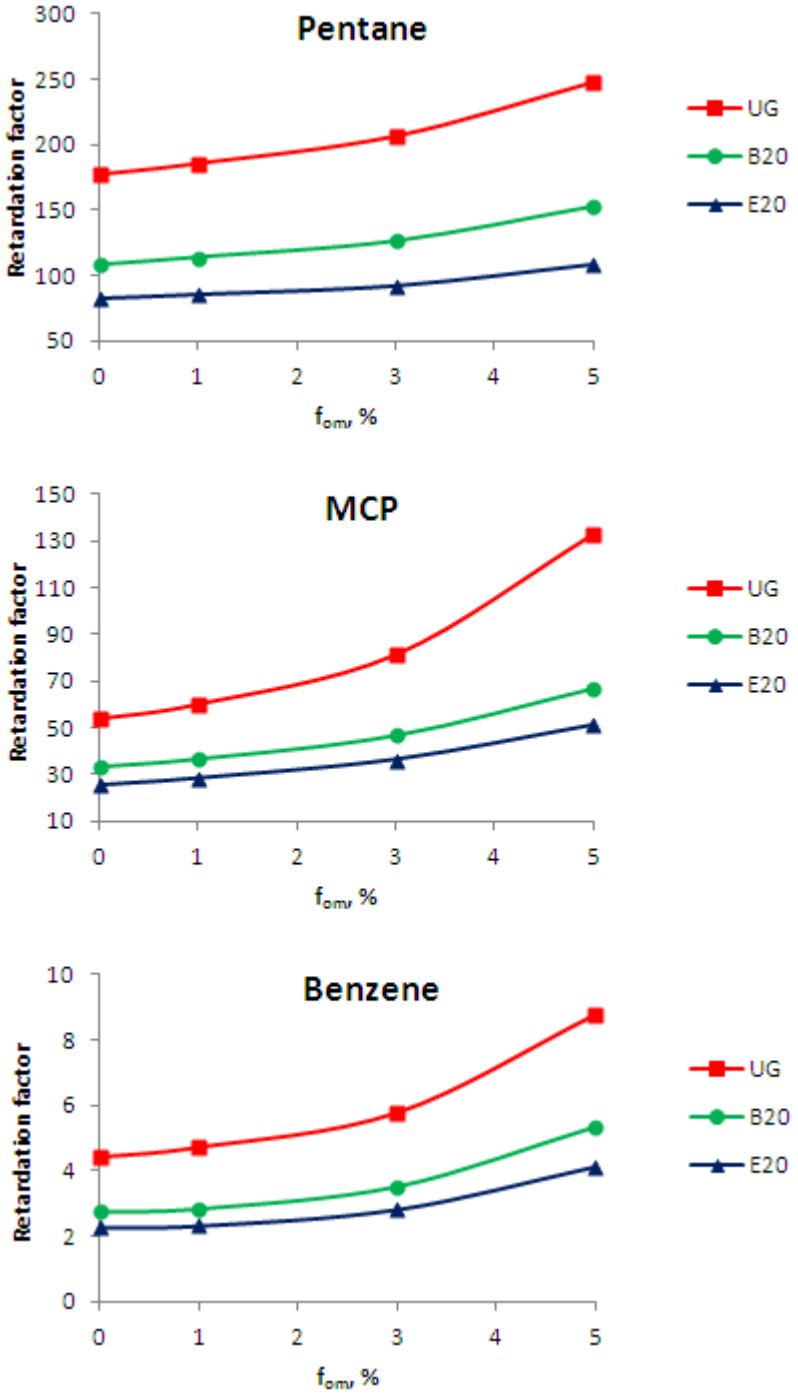

Figure 7.3 Retardation factor (R) of gasoline compounds with increasing SOM fraction of soils as a function of gasoline composition.

7.2.1.4 Mass distribution of gasoline compounds between vadose zone phases

The mass of a representative gasoline compound in the soil water, soil air and soil solids with increasing SOM fraction of soils as a function of gasoline composition is presented in Table 7.1. The mass distribution of pentane in $0\%f_{om}$ and $5\%f_{om}$ has been chosen to reduce complexity. The addition of alcohol to gasoline caused an increase in the mass of pentane distributed to the mobile phases (soil air and soil water), but reduced the mass distributed to the immobile soil solid phase. Although this effect was observed throughout the experimental duration, it was greatest on Day 1 and affected the E20 gasoline compounds to a greater extent than the B20 gasoline compounds. This strengthens the earlier observation that E20 gasoline compounds will cause greater groundwater contamination than B20 gasoline compounds.

The increase in the SOM fraction of soils generally promoted the adsorption of pentane on the soil solids, but reduced its concentration in the soil water and soil air. This effect was greatest on Day 1 and affected the E20 gasoline compounds to a greater extent compared with the B20 gasoline compounds. However, despite such higher effect on E20, the order of adsorption for the $5\%f_{om}$ soil was still the same as with $0\%f_{om}$, UG>B20>E20. More so, the concentrations of pentane in the soil air and soil water for both the $0\%f_{om}$ and $5\%f_{om}$ soils were still in the same order as E20>B20>UG. This observation indicates that SOM is unlikely to change the order of mass distribution to the vadose zone phases for different gasoline blends. This further implies that groundwater contamination with gasoline compounds will always be higher for E20 than for B20 regardless of the SOM content of soils.

Overall, the mass distribution data have shown that B20 is more likely to have a higher mass distribution to the immobile phase and a lower mass distribution to the mobile phases than E20. This indicates that ethanol-blended fuels are more likely to cause greater groundwater contamination compared to butanol-blended fuels after spills.

Table 7.1 Mass distribution of pentane between vadose zone phases with increasing SOM fraction of soils as a function of gasoline composition.

Day	UG			B20			E20		
	Solid %	Air %	Water %	Solid %	Air %	Water %	Solid %	Air %	Water %
				0%f_{om}					
1	66.3	33.6	0.1	51.6	48.3	0.2	33.6	66.2	0.3
8	71.7	28.1	0.1	58.7	40.8	0.2	56.7	42.8	0.2
15	72.5	27.0	0.1	66.6	32.8	0.1	58.6	40.6	0.2
				5%f_{om}					
1	80.7	19.2	0.1	71.9	28.0	0.1	59.5	40.4	0.2
8	83.5	16.3	0.1	75.9	23.8	0.1	70.3	29.3	0.1
15	86.1	13.7	0.1	79.6	19.9	0.1	75.4	24.0	0.1

7.2.2 Impact of soil water content on SOM sorptive capability for different gasoline blends

7.2.2.1 Sorption of gasoline compounds

Figure 7.4 compares the headspace vapour concentrations of UG, B20 and E20 representative gasoline compounds for 0, 4.5 and 9% w/w water contents for a 5%f_{om} soil. The increase in the soil water content increased the headspace concentrations of all compounds, indicating a general decrease in the sorption of all compounds by the soil. The addition of alcohol to gasoline resulted in a decreased sorption of the gasoline

compounds for all soil water contents tested. Among the alcohols, ethanol caused a greater decrease in sorption than butanol. Consequently, the E20 gasoline compounds were generally sorbed to a lesser extent by the soil compared with the B20 gasoline compounds for all soil water contents. This suggests that the sorption of gasoline compounds by soils after spills is likely to be lesser for the E20 than B20 at all soil water contents. The difference in sorption between the E20 and B20 gasoline compounds for the different soil water contents on Day 8 when sorption equilibrium can reasonably be assumed ranged from 13% for aromatics to 58% for alkanes for 0% w/w water content, from 3% for aromatics to 23% for alkanes for 4.5% w/w water content and from 2% for aromatics to 8% for alkanes for 9% w/w water content. The increase in the headspace concentrations of the gasoline compounds with increasing soil water content was in the order of E20>B20>UG. The differences in the increase in the headspace concentrations with increasing soil water content between the E20 and B20 gasoline compounds were 2.24 mg/L for alkanes, 0.44 mg/L for cycloalkanes and <0.1 mg/L for aromatics for 0% to 4.5% w/w water content increase and 0.96 mg/L for alkanes, 0.39 mg/L for cycloalkanes and <0.1 mg/L for aromatics for 0% to 9% w/w water content increase. Therefore, the data show that the increase in soil water content is likely to have greater adverse impact on the sorption of the ethanol-blended gasoline compounds than on the sorption of the butanol-blended gasoline compounds after spills.

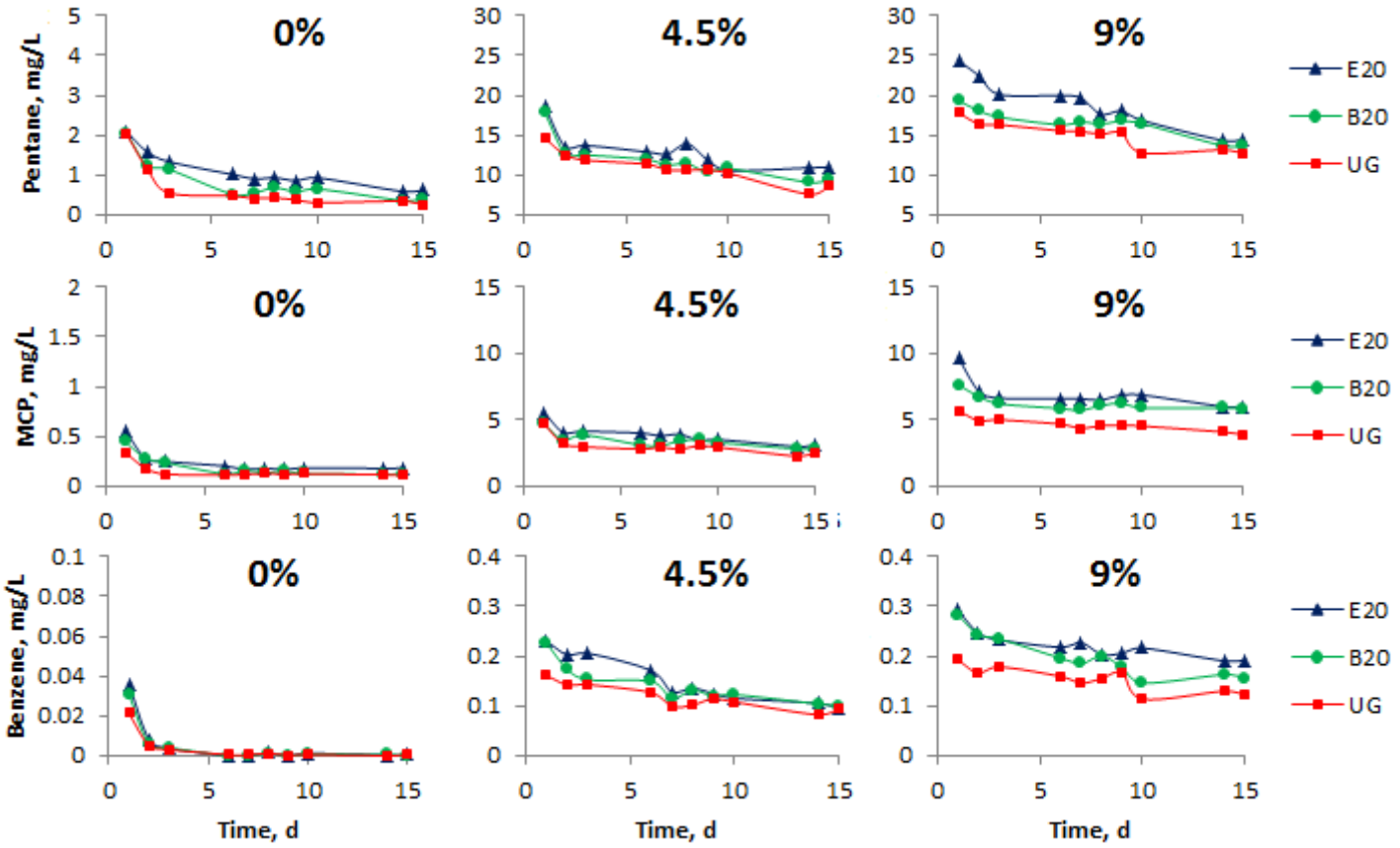

Figure 7.4 Impact of soil water content on the headspace vapour concentrations of gasoline compounds as a function of gasoline composition.

7.2.2.2 Soil-water interaction of gasoline compounds

Figure 7.5 shows the average K_d values for the UG, B20 and E20 gasoline compounds in 5%f_{om} at 0, 4.5 and 9% w/w water addition. The K_d of all compounds decreased with increasing soil water content, implying a general decrease in the adsorption of the gasoline compounds on the soil solids or increase in dissolution into the soil water. The addition of alcohol to gasoline resulted in further reductions of the K_d values for all gasoline compounds. This impact was generally greater for ethanol than butanol. Accordingly, K_d values for gasoline compounds were generally in the order of UG>B20>E20 for all the soil water contents tested. For a feasible soil water content increase from 4.5 to 9%, the K_d of B20 gasoline compounds decreased from 106.3 to 66.8 L/kg for alkanes, 59.6 to 29.1 L/kg for cycloalkanes and 2.7 to 1.9 L/kg for aromatics. In contrast, the K_d of E20 gasoline compounds decreased from 91.0 to 47.3 L/kg for alkanes, 52.8 to 22.0 L/kg for cycloalkanes and 2.5 to 1.4 L/kg for aromatics. Overall, the data indicate that an increase in soil water content could reduce the sorptive capability of soils for gasoline compounds. At all soil water contents, ethanol-blended gasoline is more likely to be adsorbed less than butanol-blended gasoline.

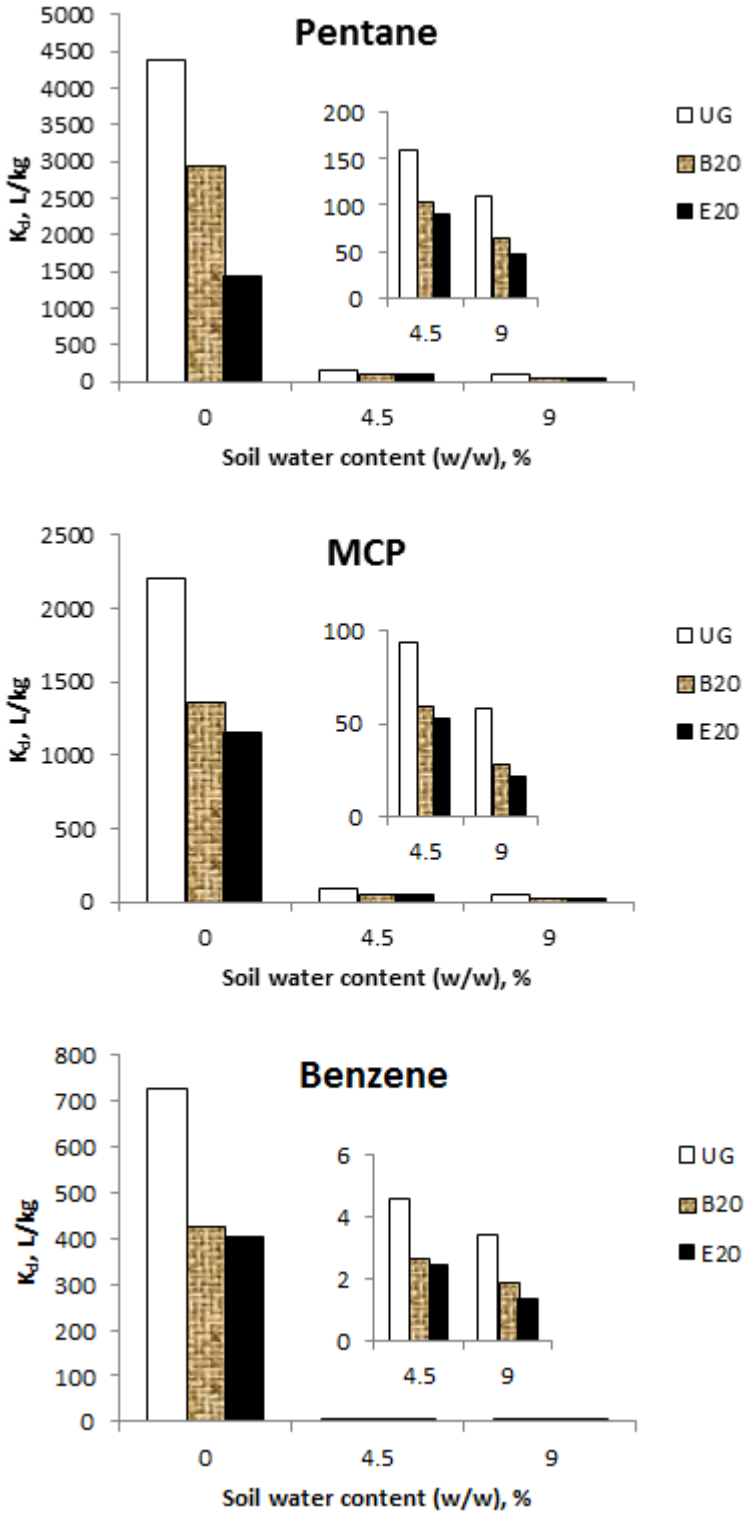

Figure 7.5 Average sorption coefficient (K_d) of gasoline compounds with increasing soil water content as a function of gasoline composition.

7.2.2.3 Mass distribution of gasoline compounds between vadose zone phases

Table 7.2 lists the mass percentages of pentane in the soil solid, soil air and soil water of a 5%f_{om} soil with increasing water content as a function of gasoline composition. Pentane was chosen to illustrate how a highly hydrophobic compound with normally low groundwater contamination problems could become a concern with the addition of alcohol to gasoline. The behaviours of the other representative gasoline compounds, MCP and benzene, followed similar trend as the pentane presented here (see Sections 5.2.4.3 and 6.2.4.3). The increase in soil water content generally reduced the adsorption of pentane for all blends on the soil solids but increased their partitioning to the soil air and soil water. This reduction was greater in the presence of alcohol. Among the alcohols, the reduction was greater in the presence of ethanol than butanol. The mass distribution trend of E20-pentane and B20-pentane at the different soil water contents shows that at very low soil water content (0 - 4.5% w/w) the distribution of the ethanol-blended and butanol-blended gasoline compounds between the vadose zone phases could be relatively similar, but could vary greatly as soil water content increases. Soil water contents of 9% and higher are more realistic in nature than those of 0 - 4.5%, suggesting that a great difference is likely to exist between the phase distributions of ethanol-blended and butanol-blended gasoline in natural vadose zone. Overall, the data indicate that an increase in the soil water content is likely to cause greater mass transfer of ethanol-blended gasoline compounds to the mobile phases and lower mass transfer to the immobile phase compared with the mass distribution of butanol-blended gasoline compounds. This implies greater risk of groundwater contamination with ethanol-blended gasoline compounds compared with butanol-blended gasoline compounds after spills.

Table 7.2 Mass distribution of pentane between vadose zone phases with increasing soil water content as a function of gasoline composition.

Day	UG			B20			E20		
	Solid %	Air %	Water %	Solid %	Air %	Water %	Solid %	Air %	Water %
				0% water content					
1	97.58	2.42	0.00	96.72	3.28	0.00	96.80	3.20	0.00
8	99.48	0.51	0.00	98.90	1.09	0.00	98.65	1.33	0.00
15	99.69	0.30	0.00	99.34	0.64	0.00	98.84	1.13	0.00
				4.5% water content					
1	83.46	16.50	0.03	72.93	27.01	0.06	73.04	26.91	0.06
8	87.91	11.95	0.02	82.48	17.32	0.04	80.97	18.80	0.04
15	90.51	9.69	0.02	85.56	14.16	0.03	82.40	17.28	0.04
				9% water content					
1	80.71	19.20	0.08	71.90	27.98	0.12	59.46	40.36	0.18
8	83.48	16.32	0.07	75.87	23.80	0.10	70.28	29.27	0.13
15	86.04	13.68	0.06	79.66	19.90	0.09	75.46	23.96	0.10

7.3 Mini-lysimeter experiments

7.3.1 Vapour phase transport of gasoline blends in the vadose zone

Figure 7.6 compares the depth profiles of the vapour phase concentrations of pentane on Days 1, 4, 8, 12 and 15 after contamination in the mini-lysimeter as a function of the gasoline composition. Pentane was chosen because it is the most volatile gasoline compound and, hence migrates faster, farthest and represents the worst case vapour phase transport scenario. The concentration profiles are shown for the selected sampling days to reduce the number of plots to be presented. All experiments were conducted with a 5%f_{om} soil, which has the highest porosity and promotes vapour phase transport better than the other soils used in this study. The vapour phase concentrations of pentane from all gasoline blends decreased with time due to adsorption on the soil solids and partitioning to the soil water. A constant rate transport of pentane from the source zone to the lower sections of the vadose zone, denoted by a horizontal concentration profile, was generally attained for all gasoline blends on Day 4. The deviation from this constant rate transport started on Day 8 for UG and B20 and on Day 12 for E20 probably due to increased adsorption on the soil solids and partitioning to the soil water.

The addition of 20% alcohol by volume to gasoline generally promoted the vapour phase concentration of pentane from Day 1 for E20 and from Day 4 for B20. It also promoted transport to the groundwater zone, however, with E20 impacted to a greater extent than B20. B20-pentane displayed series of specific behaviours with time. Between Day 1 and Day 4 the B20-pentane behaved similar to the UG-pentane, but between Day 8 and Day

12 it behaved closer to the E20-pentane. Generally, the transport behaviour of B20-pentane was midway between E20-pentane and UG-pentane. Theoretically, E20 and B20 should partitioned more into the soil water than UG due to the cosolvent effect of alcohol (Adam et al., 2002; Chen et al., 2008; Corseuil et al., 2004; Reckhorn et al., 2001), and UG should be adsorbed more on the soil solids than B20 and E20 due to its higher hydrophobicity (Weber Jr et al., 1991). Therefore, the observed lower vapour phase concentration and transport for UG-pentane suggests that more adsorption on the soil solids than partitioning to the soil water of pentane occurred in this study. The consistent higher vapour phase concentration of the E20-pentane in both the vadose zone and the groundwater zone indicates that E20 gasoline compounds could migrate faster and farther than B20 gasoline compounds after a spill. This implies that the E20 gasoline compounds could pose greater risk of groundwater contamination than B20 gasoline compounds. In general, Figure 7.6 indicates that the transport of gasoline compounds in the vadose zone as well as the risk of groundwater contamination with gasoline compounds after a spill of gasoline is likely to be in the order of UG<B20<E20.

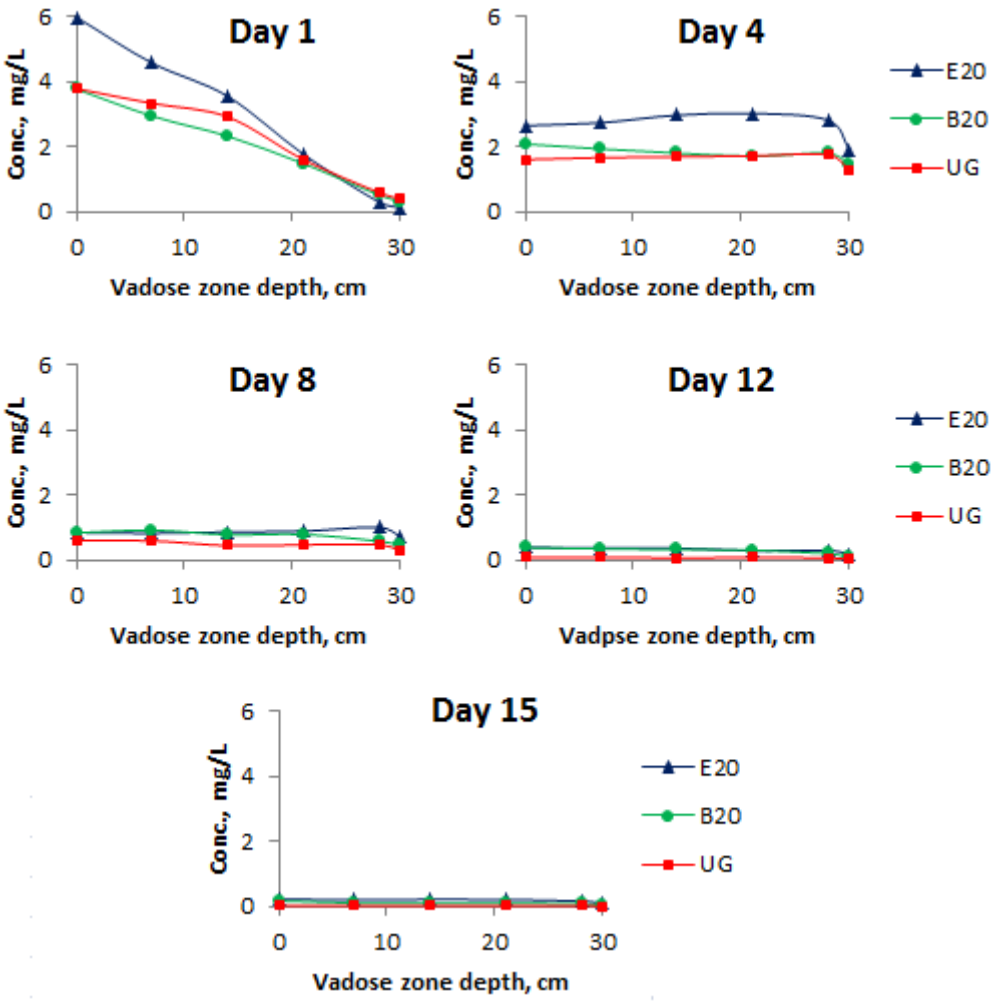

Figure 7.6 Vapour phase transport of pentane in 5%f_{om} as a function of gasoline composition.

7.4 Summary of findings

The addition of 20% alcohol by volume to gasoline reduced the sorption, retardation and mass distribution to the soil solids of all gasoline compounds. These reductions were higher for E20 than B20, suggesting that the use of E20 as transportation fuel could result in greater risk of groundwater contamination with gasoline compounds than the use of B20. Compared with the K_d of UG gasoline compounds, the K_d of E20 gasoline compounds decreased by 54% for pentane, 54% for MCP and 63% for

benzene, while the K_d of B20 gasoline compounds decreased by 39% for pentane, 38% for MCP and 49% for benzene. The retardation factor (R) of E20 gasoline compounds decreased by 53% for pentane, 53% for MCP and 48% for benzene, while the R of B20 gasoline compounds decreased by 39% for pentane, 37% for MCP and 38% for benzene. Generally, the transport of gasoline compounds in the vadose zone as well as the risk of groundwater contamination with gasoline compounds after a spill of gasoline is more likely to be in the order of UG<B20<E20.

Although soils with high SOM content could significantly reduce the degree of groundwater contamination with alcohol-blended gasoline compounds, the difference in groundwater contamination potential between ethanol-blended gasoline and butanol-blended gasoline is unlikely to be eliminated. Consequently, the K_d and R of all gasoline compounds for all soils tested were in the order of UG>B20>E20, indicating that the E20 gasoline compounds are likely to be least adsorbed and retarded by SOM.

The increase in soil water content reduced the adsorption of the alcohol-blended gasoline compounds in the vadose zone. This reduction was greater for the ethanol-blended gasoline compounds than for the butanol-blended gasoline compounds. The increase in soil water content also changed the phase distribution of the alcohol-blended gasoline compounds in the vadose zone. The ethanol-blended gasoline compounds had greater mass transfer to the mobile phases and lower mass transfer to the immobile phase compared with the mass distribution of the butanol-blended gasoline compounds. This indicates greater risk of groundwater contamination with the ethanol-blended gasoline compounds than with the butanol-blended gasoline compounds after spills.

CHAPTER EIGHT

8. CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The contamination of groundwater by gasoline compounds is attracting growing concern due to the importance of groundwater as a major drinking water resource. Consequently, it has become imperative to carefully investigate if any change in the gasoline composition, particularly the recent trend in increase ethanol or butanol content, will increase the risk of groundwater contamination. This work has contributed towards the understanding of the sorption, phase distribution and transport of ethanol and butanol blended gasoline in the vadose zone following a spill or leak as summarized below.

The addition of alcohol to gasoline reduced the sorption of gasoline compounds by soils. This effect was greatest on the first day of contamination, and affected the gasoline compounds in decreasing order of hydrophobicity. The presence of alcohol also altered the mass distribution of gasoline compounds between the vadose zone phases to higher molecular mass compounds in the mobile phases (soil air and soil water) and lower molecular mass compounds in the immobile soil solid phase. The higher molecular mass gasoline compounds in the mobile phases represent higher risk of groundwater contamination. These effects were higher for ethanol than butanol, where the average sorption coefficient (K_d) of B20 gasoline compounds decreased by 39% for alkanes, 38% for cycloalkanes and 49% for aromatics, while the K_d of E20 gasoline compounds reduced by 54% for alkanes, 54% for cycloalkanes and 63% for aromatics.

Generally, the transport of gasoline compounds from the vadose zone to the groundwater zone was found to be in the order of E20>B20>UG, indicating that the risk of groundwater contamination with gasoline compounds after a spill or leak is more likely to be greater for ethanol-blended gasoline than butanol-blended gasoline.

The addition of SOM to sand increased its sorption capability and thereby reduced the risk of groundwater contamination with alcohol-blended gasoline compounds. This effect was found to be similar for ethanol and butanol blended gasoline as the K_d of E20 and B20 gasoline compounds were equally increased 7 times for aromatics, 4 times for cycloalkanes and 2 times for alkanes, for 0 to 5% increase in the SOM fraction of sand. Therefore, the impact of SOM is unlikely to alter the order of groundwater contamination risk for ethanol and butanol blended gasoline. Accordingly, the K_d of gasoline compounds for all SOM fractions tested, including $0\%f_{om}$, $1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$, were in the order of UG>B20>E20, indicating greater risk of groundwater contamination for the ethanol-blended gasoline after a spill or leak regardless of the SOM content of the soil.

The increase in the water content of soils reduced the sorptive capability of SOM in soils and thus affected the overall mass distribution of gasoline compounds between the soil solid, soil air and soil water phases. This implies that the degree of gasoline compounds retention in the vadose zone by SOM could differ during the dry summer and wet winter seasons. Although similar sorption trend was observed for the B20 and E20 gasoline compounds at all soil water contents tested, the sorption of the B20 gasoline compounds were generally higher than the sorption of the E20 gasoline compounds as evident in the B20 gasoline compounds K_d of 2,954.7, 106.3 and 66.8 L/kg for alkanes, 1,370.1, 59.6 and 29.1 L/kg for

cycloalkanes and 428.8, 2.7 and 1.9 L/kg for aromatics compared with the E20 gasoline compounds K_d of 1,427.5, 91.0 and 47.3 L/kg for alkanes, 1,160.4, 52.8 and 22.0 L/kg for cycloalkanes and 405.1, 2.5 and 1.4 L/kg for aromatics, at 0, 4.5 and 9% w/w soil water content, respectively. Thus, in both the dry and wet seasons, the amount of gasoline compounds retained by SOM in the vadose zone is more likely to be higher for butanol-blended gasoline than ethanol-blended gasoline.

Generally, all results indicated that the use of butanol as gasoline oxygenate would result in lesser risk of groundwater contamination with gasoline compounds compared with the use of ethanol. Therefore, to successfully reduce greenhouse gases emissions via high alcohol volume in gasoline and still protect the world's groundwater resource, this study suggests the use of butanol rather than ethanol.

8.2 Recommendations

This work has focused on the sorption, phase distribution and transport of the vapour phase of ethanol and butanol blended gasoline in the vadose zone using microcosm and mini-lysimeter. The choice of vapour phase was prompted by the importance of the vapour phase of contaminants in predicting their behaviour and fate in the subsurface environment (Lyman et al., 1990). However, the mini-lysimeter experiment can be extended to include water phase and solid phase extraction to obtain additional information on the fate of ethanol and butanol blended gasoline in the subsurface environment. Such additional information may include:

- Amount of gasoline compounds retained in the various vadose zone phases at the end of the experiment.

- Contribution of each mobile phase transport towards groundwater contamination.
- Rainfall effect on the transport of gasoline compounds to the groundwater.

In addition to the sorption, phase distribution and transport of gasoline in the subsurface environment, the work can also be extended to cover areas such as:

- Biodegradation of gasoline compounds in the vadose zone.
- Attenuation of gasoline compounds in groundwater.
- Microbial population estimation.

Extending this work to incorporate biodegradation would provide a more comprehensive knowledge of the natural attenuation of gasoline compounds in the subsurface environment following release of ethanol and butanol blended gasoline. This is particularly important as it has been reported that the toxicity of alcohols increases with increasing hydrophobicity, and that the short-chain alcohols are less toxic than the more hydrophobic longer-chain alcohols (Ulrich, 1999).

Finally, while the results of this work suggest that the risk of groundwater contamination would be less for butanol-blended gasoline relative to ethanol-blended gasoline, field data would help develop a stronger argument for this observation. Therefore, a field-scale test is recommended to validate in the field processes observed in the laboratory and to calibrate predictive models of the long-term net flux of ethanol and butanol blended gasoline compounds into groundwater.

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APPENDICES

Appendix A Generation of raw data from experiments and necessary calculations carried out.

This appendix provides a detailed explanation of how the data used in this study were generated from the microcosm and mini-lysimeter experiments described in Sections 3.3 and 3.4, respectively. It explains, where necessary, how samples were extracted and analysed. Finally, it itemised the different calculations performed on the raw data obtained using a gasoline compound from a selected experiment.

1 Microcosm experiment calculations

1.1 Concentration

Generally, data were generated from the batch microcosm experiments by injecting 40 µL headspace samples into the GC-FID. The peak area obtained from each GC-FID analysis was recorded and used to estimate the mass of each gasoline compound in the analysed sample via the calibration equation and the peak area relationship of each compound (see Figure 4.1). The concentration of each gasoline compound in the analysed sample was calculated by dividing the estimated mass with the volume of sample injected into the GC-FID (40 µL). An illustration of this calculation is presented below for pentane on the Day 1 of UG experiment with 5%f_{om} soil.

Calibration equation: y = 5E+11x

Volume of sample injected: 40 µL

Areas of pentane obtained from 3 microcosms (y):

Microcosm 1 = 329951.58 µVs

Microcosm 2 = 362394.30 µVs

Microcosm 3 = 376328.16 µVs

Average area of pentane obtained (y): 356224.68 µVs

The mass of pentane was calculated using the calibration equation for pentane (see Figure 4.1):

Mass of pentane injected (x) = y / 5E+11

= 356224.68 / 5E+11

= 7.12449E-07 g

Therefore, concentration of pentane = x / volume injected

= 7.12449E-07 g / 40 µL

= 1.7811E-08 g/µL

= **17.81 mg/L**

1.2 Mass distribution

The mass of gasoline compounds that partitioned to the soil air, soil water and soil solid phases of the vadose zone were estimated using Equations [2.8], [2.9] and [2.10 or 2.11], respectively. To demonstrate how these estimates were made, the same pentane data from UG experiment with 5%f_{om} soil is used.

Mass of pentane in air (M_a) = C_a * V_a

C_a (Concentration in air) = 17.81 mg/L (on Day 1) = 1.7811E-05 g/mL

V_a (Volume of air in microcosm) = Headspace vol. + Soil air vol.

Headspace vol. = Total microcosm vol. – Total soil vol. (V_{ts})

= 60 ml - $\prod r^2 h$

= 60 ml – 3.14 * 1.375^2 * 10

= 0.63 mL

Soil air vol. = Volumetric air porosity (θ_a) * V_{ts}

But θ_a = Total porosity (θ_t) – Volumetric water content (θ_w)

θ_t = 1 – Soil solid porosity (θ_s)

Firstly, θ_w is calculated:

θ_w = Water content vol. (V_w) / V_{ts}

% water content by mass in soil = 9%

Total soil mass = 65 g

Therefore, water content in soil = 0.09 * 65 g = 5.85 g

V_w = 5.85 g / 1 g/mL (density of water) = 5.85 mL

Thus, θ_w = 5.85 / 59.37 = 0.10

Secondly, θ_s is calculated:

θ_s = Vol. of soil solid / V_{ts}

Vol. of soil solid = Mass of soil solid / Soil particle density

(From Table 4.4 soil particle density, ρ_s = 2.1)

Mass of soil solid = Total soil mass – water content

= 65 – 5.85 = 59.15 g

Vol. of soil solid = 59.15 / 2.1 = 28.17 mL

Hence, θ_s = 28.17 / 59.37 = 0.47

Thirdly, θ_t is calculated:

$\theta_t = 1 - \theta_s = 1 - 0.47 = 0.53$

Fourthly, θ_a is calculated:

$\theta_a = \theta_t - \theta_w = 0.53 - 0.10 = 0.43$

Therefore, soil air vol. = $\theta_a * V_{ts} = 0.43 * 59.37 = 25.53$ mL

Then, $V_a = 0.63 + 25.53 = 26.16$ mL

Finally, the mass of pentane in air (M_a)

= $C_a * V_a$ = 1.7811E-05 g/mL * 26.16 mL

= 4.6593576E-04 g = **465.94 µg**

Mass of pentane in water (M_w) = (C_a / H) * V_w

C_a = 1.7811E-05 g/mL

H (Henry's law constant for pentane) = 51.4 (from Table 3.1)

V_w (Vol. of water in microcosm) = 5.85 mL

Therefore, M_w = (1.7811E-05 g/mL / 51.4) * 5.85 mL

= 2.0271E-06 g = **2.03 µg**

Mass of pentane in solid (M_s) = M_t – M_a - M_w - M_L

M_a = 465.94 µg

M_w = 2.03 µg

M_t (Total mass of pentane injected into microcosm)

= 2.43E-03 g (from Table 3.3)

= 2.43E+03 µg

M_L (Mass lost via sampling) = 0 µg on Day 1

Therefore, M_s = 2.43E+03 µg - 465.94 µg - 2.03 µg = **1962.03 µg**

1.3 Sorption coefficient

The sorption coefficient (K_d) of each gasoline compound was estimated using Equation [2.12 or 2.15]. K_d was estimated for each sampling day and the average K_d was used as the representative K_d. The standard deviation of all the K_d was calculated and used as the error bar. The K_d calculation procedure is illustrated with the same pentane data used in the preceding sections.

Using Equation [2.12], K_d for Day 1 = C_s (Day 1) / C_w (Day 1)

C_s (Conc. of pentane in solid) = M_s / Total soil mass

= 1962.03 µg / 65 g = 30.19 µg/g

C_w (Conc. of pentane in water) = Conc. of pentane in air (C_a) / H

But C_a on Day 1 = 1.7811E-05 g/mL = 17811 µg/L

Then, C_w = 17811 µg/L / 51.4 = 346.52 µg/L

Therefore, K_d for Day 1 = 30.19 µg/g / 346.52 µg/L

= 0.087123 L/g = **87.12 L/kg**

Using Equation [2.15], $K_d = \frac{H}{C_a M_{ts}}\left(M_t - C_a V_a - \frac{C_a V_w}{H} - M_L\right)$, also gave K_d for Day 1 as **87.12 L/kg**.

The K_d for the other experimental days were similarly calculated and are as follows:

K_d for Day 2 = 96.23 L/kg

K_d for Day 3 = 96.84 L/kg

K_d for Day 7 = 103.31 L/kg

K_d for Day 8 = 106.00 L/kg

K_d for Day 9 = 104.53 L/kg

K_d for Day 10 = 129.31 L/kg

K_d for Day 14 = 125.12 L/kg

K_d for Day 15 = 130.41 L/kg

Average K_d for pentane = **108.76 L/kg**

Standard deviation = **15.77**

1.4 Retardation factor

Equation [2.16] was used to calculate the retardation factor (R) of each gasoline compound. Using the same pentane data used in the previous sections, R of pentane in the 5%f_{om} soil was calculated as shown below.

$R = 1 + (\rho/n) K_d$

ρ (bulk density) = mass of 5%f_{om} in microcosm / V_{ts}

= 65 g / 59.37 mL

= 1.09 g/mL

n (porosity of 5%f_{om} in microcosm) = $1 - (\rho / \rho_s)$

ρ_s (particle density of 5%f_{om}) = 2.1 g/mL (from Table 4.4)

Then, n = 1 – (1.09 / 2.1) = 0.48

K_d = 108.76 L/kg = 108.76 mL/g

Therefore, R = 1 + (1.09 g/mL / 0.48) * 108.76 mL/g = **247.98**

2 Mini-lysimeter experiment calculations

2.1 Concentration

Data were generated from the mini-lysimeter experiments by auto-sampling and analysing soil gas samples from individual sampling ports using HPR-20 Mass Spectrometer as described in Section 3.4.5. The concentration (C_g) of each gasoline compound was estimated from the average of the last three stable partial pressure values obtained from the HPR-20 Mass Spectrometer analysis using the specific partial pressure-concentration relationship in Table 4.3. The concentration value obtained was adjusted by subtracting from it the specific background concentration value. This calculation is illustrated with pentane data on Day 1 for UG experiment with 5%f_{om} soil as follows:

C_g for Day 1 at source zone (0 cm)

= (Av. partial pressure * torr-g/mL relationship) – Background conc.

Where,

Av. partial pressure = 3.87E-11 torr

torr-g/mL relationship: 1 torr = 9.83E+04 g/mL (from Table 4.3)

Background conc. = Average partial pressure * torr-g/mL relationship

= 4.62E-14 * 9.83E+04 g/L

= 4.54E-09 g/mL

Therefore,

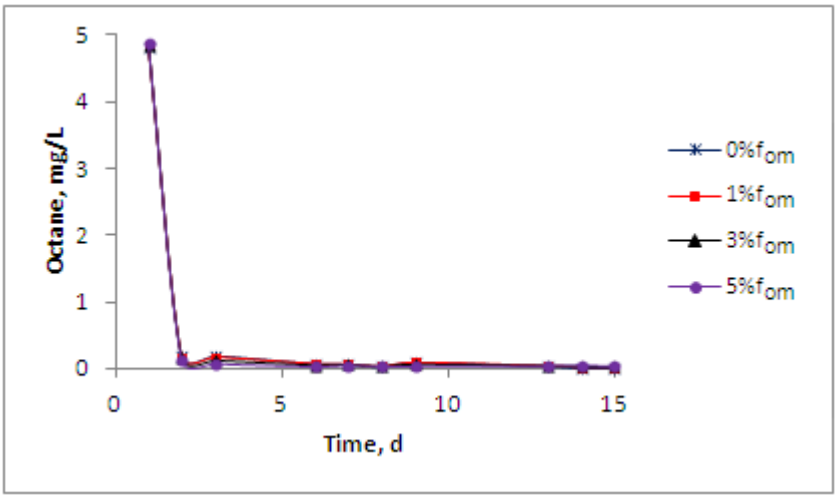
C_g for Day 1 at 0 cm = (3.87E-11 * 9.83E+04 g/mL) - 4.54E-09 g/mL

= **3.80E-06 g/mL = 3.80 mg/L**

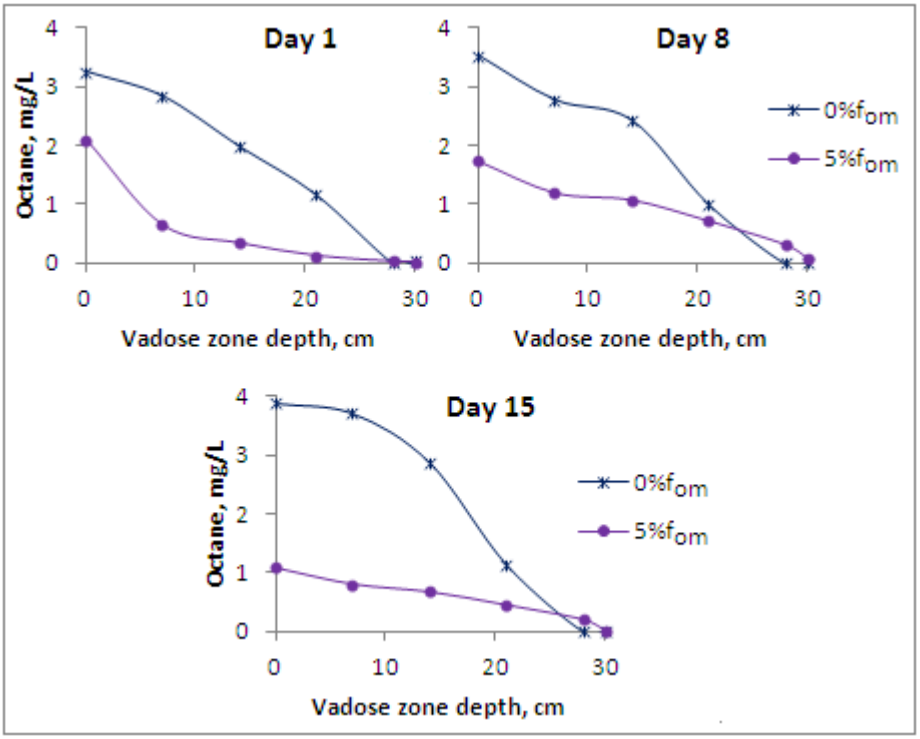
Appendix B Detection of octane by (a) GC-FID and (b) HPR-20 MS.

Appendix B shows the poor detection of octane by the GC-FID used for the microcosm experiments (a), which necessitated its exclusion from the figures of this work. The appendix also shows the reasonable detection of octane by the HPR-20 MS used for the mini-lysimeter experiments (b), which is a confirmation of the high sensitivity and hence suitability of the HPR-20 MS for gasoline compounds analysis.

(a)



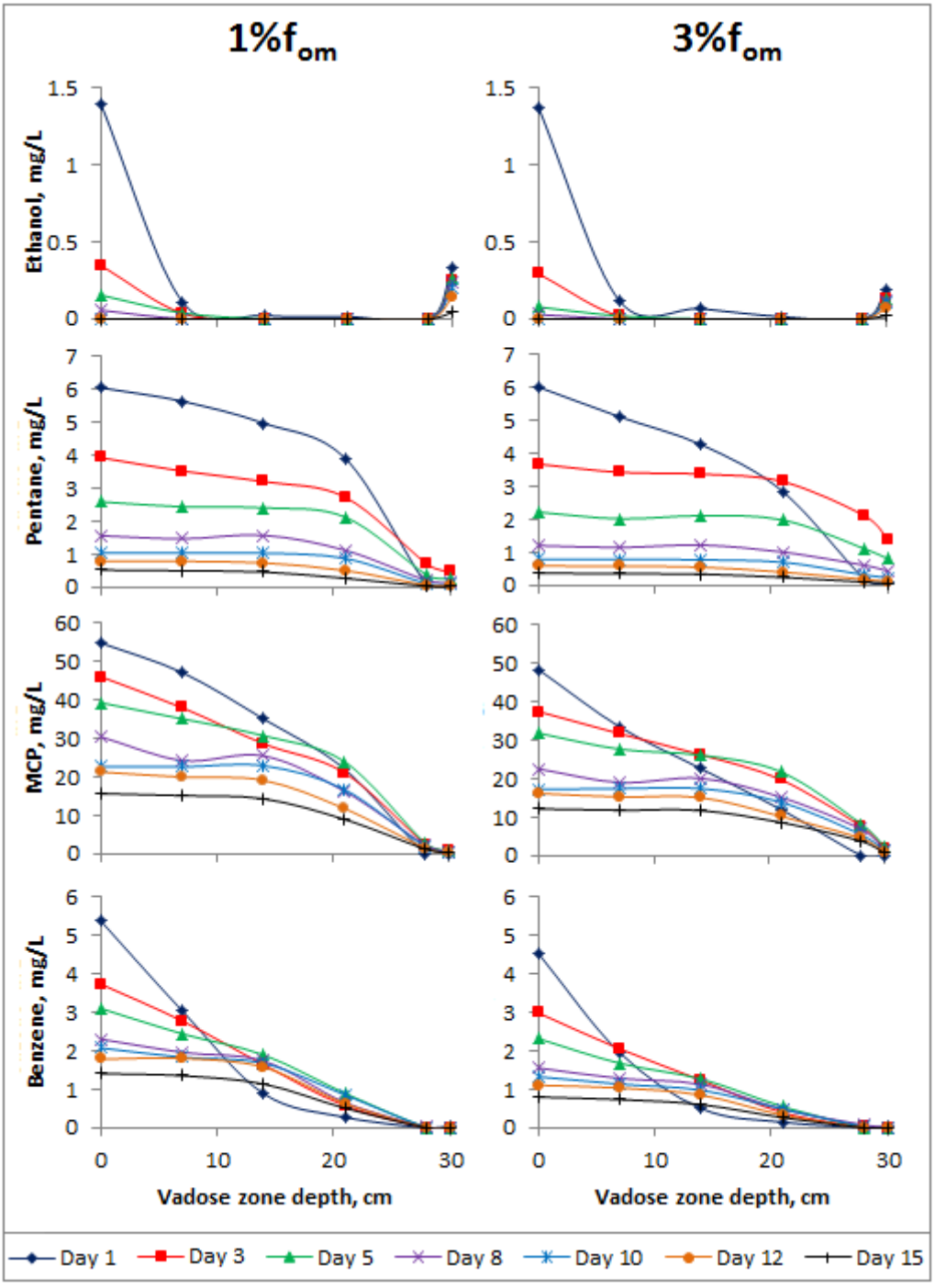
(b)



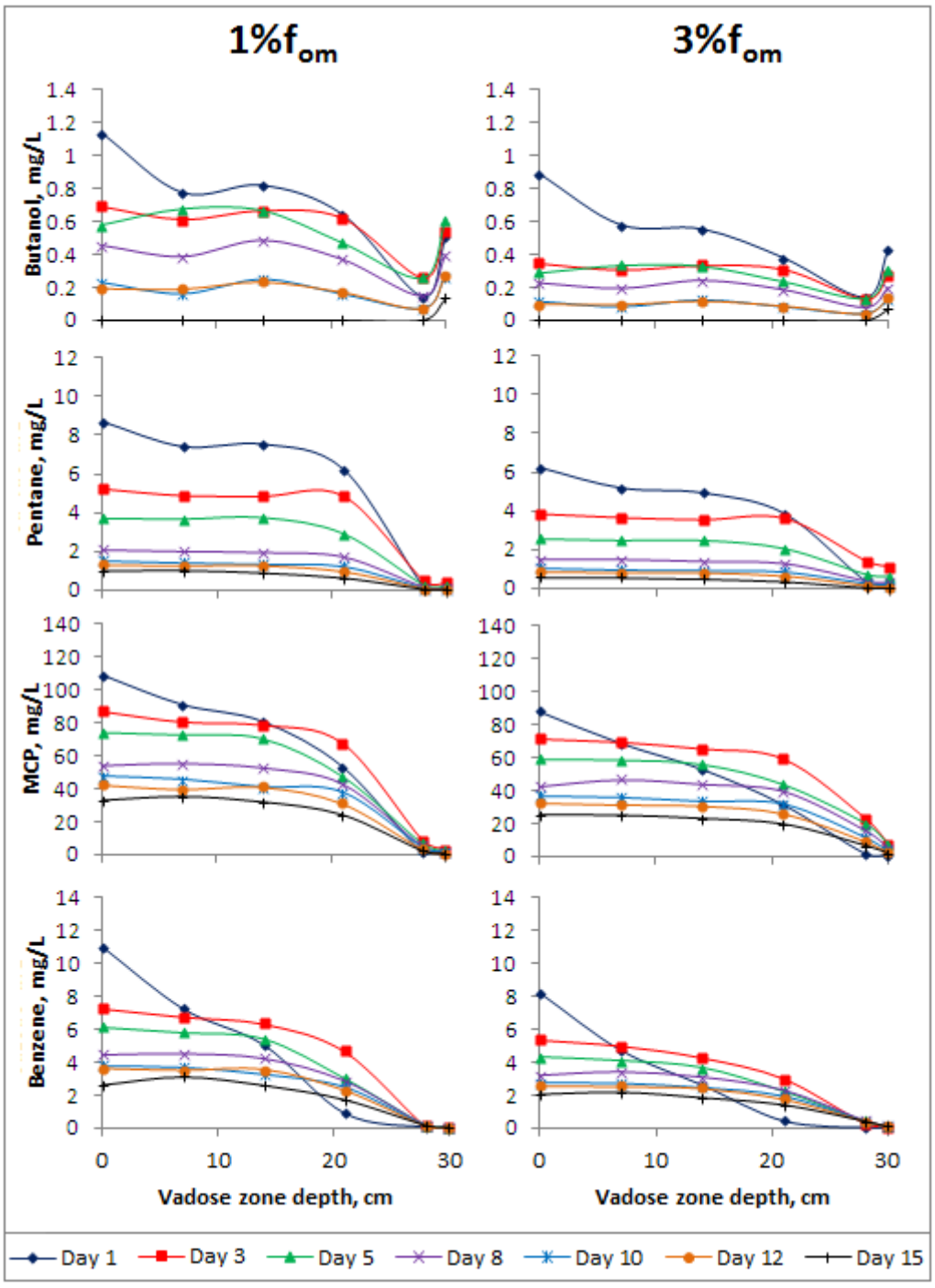
Appendix C The concentration profiles of representative gasoline compounds in 1%f_{om} and 3%f_{om} for (a) E20 and (b) B20.

This appendix presents the mini-lysimeter concentration profiles for the gasoline mixtures representative compounds in 1%f_{om} and 3%f_{om} soils which could not be included in Figures 5.9 and 6.9 in Sections 5.3.2 and 6.3.2, respectively, due to space constraint. Figure (a) presents the concentration profiles which could not be included in Figure 5.9 in Section 5.3.2, while Figure (b) presents the concentration profiles which could not be included in Figure 6.9 in Section 6.3.2. These concentration profiles in 1%f_{om} and 3%f_{om} soils exhibited behaviours that are amid those of 0%f_{om} and 5%f_{om} soils.

(a)


1%f_om
3%f_om
Ethanol, mg/L
Pentane, mg/L
MCP, mg/L
Benzene, mg/L
Vadose zone depth, cm
Vadose zone depth, cm
Day 1
Day 3
Day 5
Day 8
Day 10
Day 12
Day 15

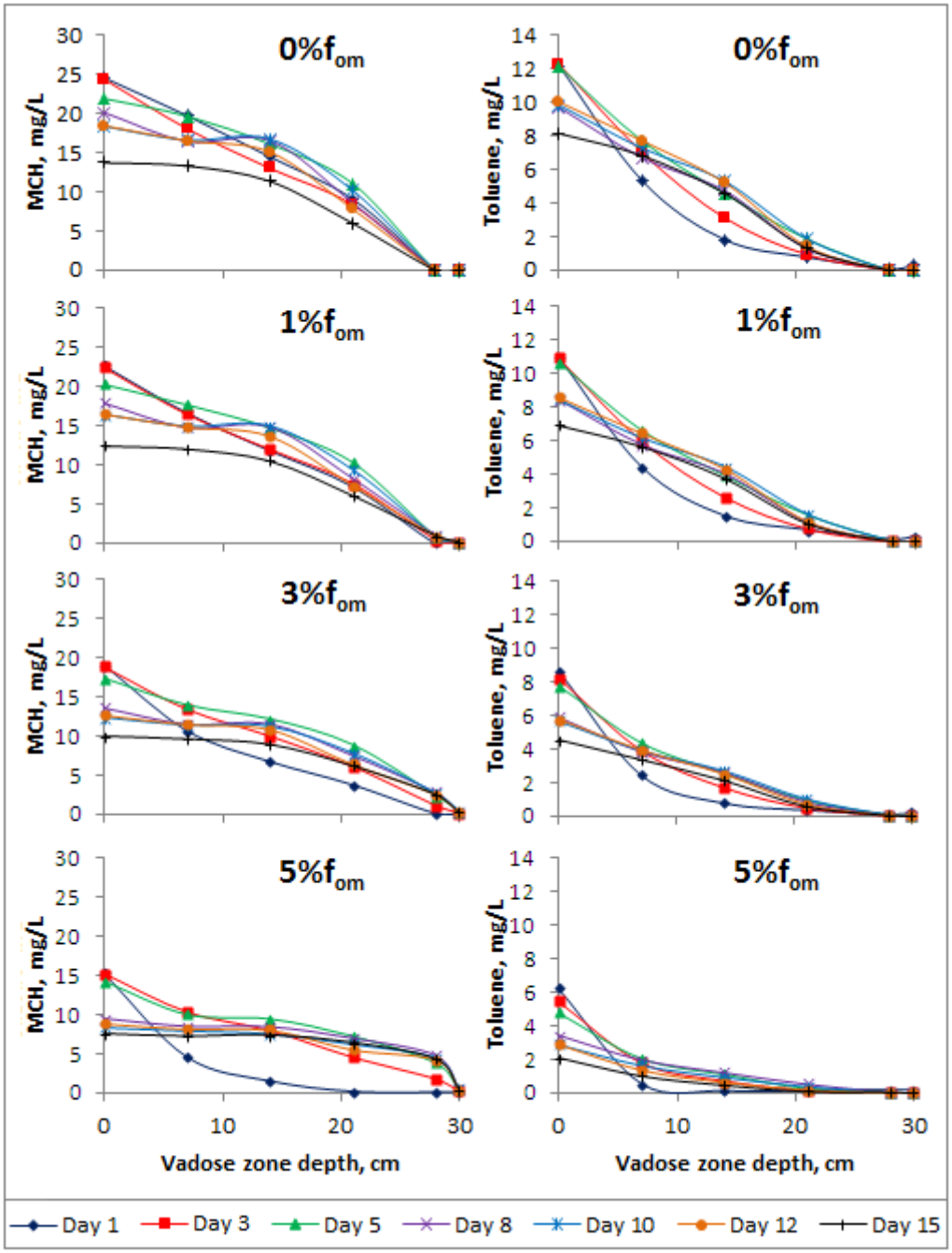
(b)


1%f_om
3%f_om
Butanol, mg/L
Pentane, mg/L
MCP, mg/L
Benzene, mg/L
Vadose zone depth, cm
Vadose zone depth, cm
Day 1
Day 3
Day 5
Day 8
Day 10
Day 12
Day 15

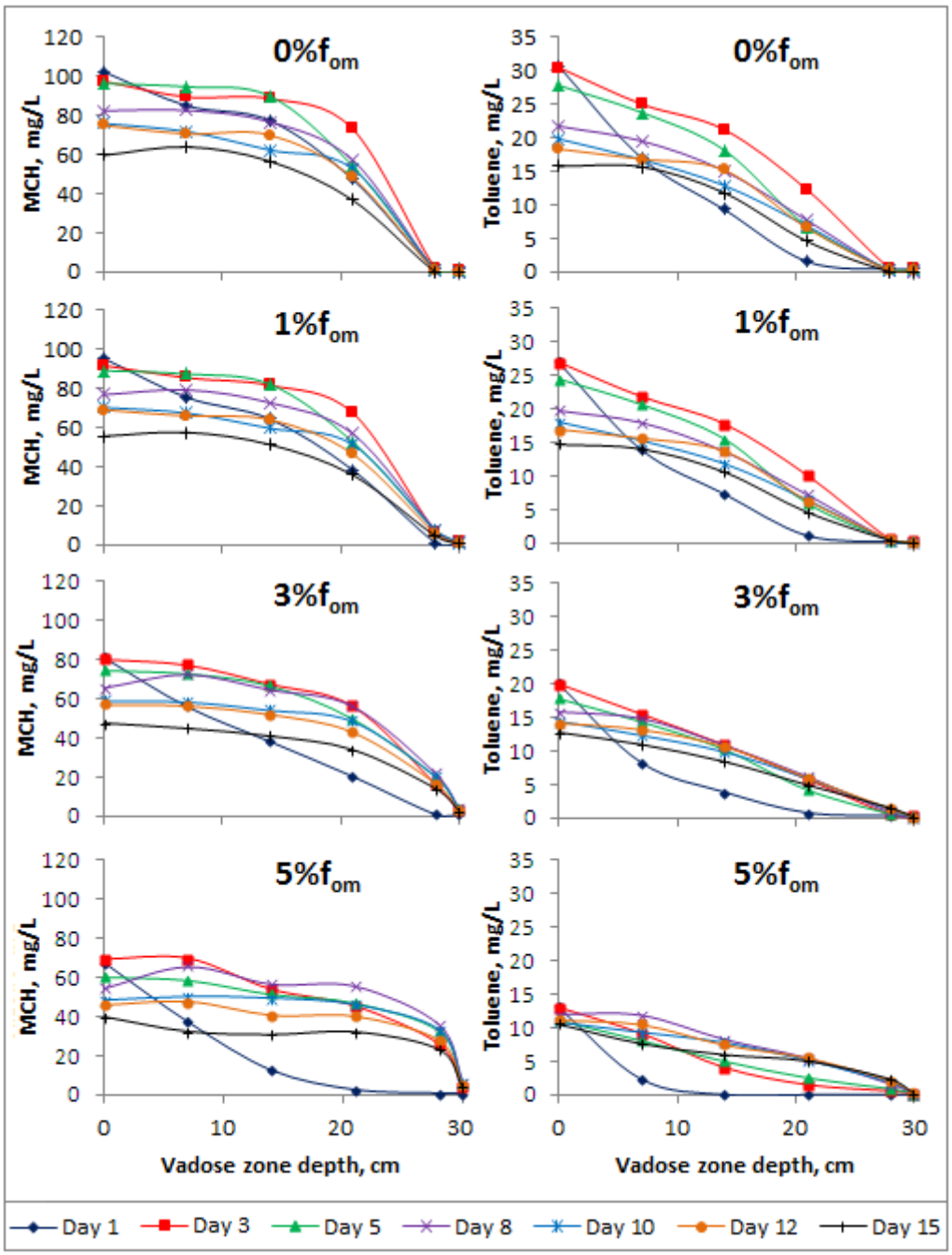
Appendix D The concentration profiles of the less volatile gasoline compounds for (a) E20 and (b) B20.

Appendix D shows the mini-lysimter concentration profiles for the less volatile gasoline compounds (toluene and MCH) of the gasoline mixtures. Figure (a) shows the concentration profiles for toluene and MCH in 20% ethanol-blended gasoline, while Figure (b) shows the concentration profiles for toluene and MCH in 20% butanol-blended gasoline. The concentration profiles for these less volatile gasoline compounds exhibited high degree of scatter probably due to suppression by the highly volatile representative compounds, thus, were not presented in Sections 5.3.2 and 6.3.2 of the ethanol-blended gasoline and butanol-blended gasoline study, respectively.

(a)


0%f_om
1%f_om
3%f_om
5%f_om
MCH, mg/L
Toluene, mg/L
Vadose zone depth, cm
Day 1
Day 3
Day 5
Day 8
Day 10
Day 12
Day 15

(b)


0%f_om
1%f_om
3%f_om
5%f_om
MCH, mg/L
Toluene, mg/L
Vadose zone depth, cm
Day 1
Day 3
Day 5
Day 8
Day 10
Day 12
Day 15

Appendix E Publications from this research.

This appendix presents the conference proceedings and journal papers that ensued from this research. It also contains anticipated journal papers that may possibly emanate from this work.

1 Conference Proceedings

Ejikeme Ugwoha and John M. Andresen (2011). Impact of ethanol on the retention of gasoline compounds in the vadose zone. Midlands Energy Graduate School (MEGS) Annual Conference, Park Inn Nottingham on 8th - 9th September 2011, Nottingham, UK.

Ejikeme Ugwoha and John M. Andresen (2012). Comparing the sorption and phase distribution of 20% ethanol- and butanol-blended gasoline compounds in the vadose zone. Urban Environmental Pollution (UEP) 2012, NH Grand Hotel Krasnapolsky on 17th – 20th June 2012, Amsterdam, Netherlands.

2 Journal Papers

Ejikeme Ugwoha and John M. Andresen, 2012. Vapour phase investigation of the impact of soil organic matter on the sorption and phase distribution of 20% ethanol-blended gasoline in the vadose zone**.** Continental Journal of Water, Air and Soil Pollution, 3 (2): 1-12.

3 Journal Papers in Review

Ejikeme Ugwoha and John M. Andresen. Impact of soil organic matter on the sorption and phase distribution of 20% butanol-blended gasoline in the vadose zone. Submitted on 17th July 2012 to International Journal of Water Resources and Environmental Engineering.

4 Journal Paper in Preparation

Ejikeme Ugwoha and John M. Andresen. Sorption and phase distribution of ethanol and butanol blended gasoline vapours in the vadose zone after release. To be submitted to Journal of Environmental Sciences.